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PROCEEDINGS OF

THE ROYAL SOCIETY.

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Address of the President, Sir Charles S. Sherrington, at the Anniversary Meeting, November 30, 1923.

At the Anniversary Meeting of the year our minds naturally revert to those of this Fellowship whom the past twelve months have taken from it.

In December last, in his eighty-third year, died **Charles Douglas Hanbury-Tracy**, 4th Baron Sudeley, naval officer and also Member of The Inner Temple. Keenly interested in science, he had given long public-spirited service to the cause of the National Museums, urging on more than one Government and at more than one period critical for their finance, the scientific and educational importance of them to the country.

Charles Immanuel Forsyth Major died on March 25. By profession a physician, by inclination a naturalist, he had spent the greater part of a long and vigorous life-time in pursuit of palæontology. To that subject his field work in Italy, Samos, Madagascar, Corsica and elsewhere brought memorable contributions. His collections went in large measure to the national collections. At the British Museum for a time he was engaged in cataloguing the fossil mammals, a chapter of palæontology on which he was a specially equipped authority.

On March 27 died at the Royal Institution, where he had been Fullerian Professor of Chemistry for 46 years, **James Dewar**, successor there to Davy and Faraday, and Director of the Research Laboratory which bears their conjoint names. Like them, a master in experimentation, his achievements ensure him a place along with theirs in the tradition of the Institution where he followed them. The Royal Society's Rumford Medal founded by the founder of the Royal Institution, was awarded to him in 1894; in later years he received from the Society its Davy Medal and its Copley Medal. His Bakerian Lecture, delivered in this room twenty-two years ago, he entitled "The Nadir of Temperature." That designation he gave to it recalls how, by evaporating liquid hydrogen under reduced pressure, he obtained hydrogen as a frozen foam and air as a rigid inert solid. The discoveries he made were some of them rich in practical application, yet it was the sheer enrichment of Natural Knowledge which engrossed his life. To a gift of scientific imagination he had added the acquisition of supreme scientific technique. His temperament was allied to that of the artist; for him a demonstrative experiment was akin to an artistic creation. By his enthusiasm for science, its possibilities, its responsibilities, and its prerogatives as he saw them, his nature was sometimes stirred in degree difficult for others to understand. Science he certainly loved, and with the ardour of an explorer for an horizon. Looking once into a friend's album I saw that, when asked to supply a sentence for it, Dewar had written: "No familiarity can reconcile our minds to the incredible properties of that something which we call matter." Those words of his own illustrate, I think, one aspect of the spirit in which he pursued research throughout his time.

JOHN VENN, President of Gonville and Caius College, and for many years Lecturer in Logic and Moral Philosophy at Cambridge, died in April in his eighty-ninth year. Probably the best-known of his contributions to science was a suggestive volume entitled "Symbolic Logic." Always devoted to his College, within whose circle almost all his life was passed, much of the work of his later years was given to writing an exhaustive biographical history of it. And besides those of his College he had issued records of much value for the history of the University itself. To those who knew him personally he stood as an attractive personification of length of years, retaining to their end an undimmed interest in the present, and seeing it kindly as wisely through the perspective of a long vista of the past.

CHARLES NIVEN, mathematician, died in May. He had been Professor of Natural Philosophy in the University of Aberdeen for forty-two years. His original contributions to mathematics date, however, chiefly to the time of his earlier Professorship, namely in the Chair of Mathematics at Cork. His work won repute for analytical skill, and he had been elected a Fellow of the Society as far back as 1880.

SYDNEY SAMUEL HOUGH, H.M. Astronomer, Royal Observatory, Cape of Good Hope. In the course of a brilliant mathematical career at Cambridge he showed mathematically how the elastic yielding of the earth caused a lengthening of the period of the latitude variation from 305 to 430 days. He revised Laplace's "Theory of the Tides" and made what Sir George Darwin described as the most important contribution to this theory since the time of

Laplace. At the instance of Sir David Gill, he was appointed Chief Assistant at the Cape in 1898 and succeeded Sir David in 1907. He built very well on the foundations which Gill had laid, and made what is probably the most valuable contribution of recent years to the determination of absolute positions of the stars in the sky. He also gave much thought to the Astrographic Catalogue and made the Cape section a very valuable contribution to this work. The publication was nearly completed when fatal illness removed him at a relatively early age.

HENRY HOYLE HOWORTH died on July 15, at the age of eighty-one. Of varied attainments, he had written extensively on themes archæological, ethnological and geological; during a lengthy period he had taken an active part in public life.

HENRY HUBERT HAYDEN, geologist, met his death while returning from a mountain ascent in Switzerland. Director of the Geological Survey in India during eleven years, he had been appointed to it in 1910. He was elected Fellow of the Society in 1915. Of outstanding personality on many counts, he was distinguished scientifically perhaps especially for his Himalayan and trans-frontier stratigraphical work. Accompanying Sir Francis Younghusband's expedition to Lhassa, the observations he then made have been described as opening a new chapter in Himalayan geology. After retiring from the Indian Government's service he again, only last year, visited Northern Thibet. His death, at the age of fifty-four, brought an untimely close to the inspiring career of one who was at once geologist, naturalist, and explorer.

In September died JOHN Viscount MORLEY, of Blackburn, prominent in politics and in letters. He had given direct service to Education as Chancellor of the University of Manchester for the last fifteen years.

HERBERT McLEOD, dying last month in his eighty-third year, had been a Fellow of the Society for 42 years. Early in his career he was Lecture Assistant at the Royal College of Chemistry, and had a part in the discovery of the aniline dye, Magenta. Later he was appointed Professor of Experimental Science (afterwards Chemistry) at the Royal Indian Engineering College, Coopers Hill. There, for measurement of low-pressure of gases, he devised the McLeod gauge, long generally in use for such work. The years of patient and sound bibliographical work he gave to the Catalogue of Scientific Papers constitute a special lien on the grateful remembrance of him by the Society. From 1888 onwards he had read the proofs for the Catalogue, and in May, 1902, he undertook the Catalogue's direction; he prepared the subject-index to its papers dating between 1800 and 1900. He had further seen the author catalogue for the period 1883–1900 half through the press when ill-health obliged him to desist from continuance of that work in 1915.

John Allen Harker died on October 10. At an early point in his research career he had carried out, in collaboration with Chappuis, an elaborate comparison of the gas and platinum thermometer scales. Selected subsequently for the staff of the then young National Physical Laboratory, he became head of the Thermometry Division of that Institution, and he was for some time Chief Assistant of it. From there issued his valued series of papers on high-temperature measurements. During the war he was responsible for the organisation of the work of the Nitrogen Products Committee of the Ministry of Munitions, and was Director of the Research Laboratories of the Inventions Department of that Ministry. He was an active member of the Oxygen Committee of the Department of Scientific and Industrial Research. In the last few years he had taken deep interest in the question of the large-scale use of oxygen-gas as a therapeutic agent. Never robust in health, and sometimes severely taxed physically during the stress of his war work, the uncertainties of his own health seemed little to abate his high-strung activity, and despite illness his scientific keenness and enthusiasm remained always with him.

Arthur Alcock Rambaut died on October 14, in his sixty-fifth year. Some time Astronomer Royal in Ireland, he had for the past six and twenty years been Observer at the Radcliffe Observatory in Oxford. His contributions to astronomical literature were numerous. A catalogue of 1,012 Southern Stars was issued by him in 1887, and in 1906 appeared his Radcliffe Catalogue. With the publication in this present year of a volume of the Radcliffe Observations containing the resulting parallaxes of 2,400 stars he had had the satisfaction of witnessing the completed issue of a main labour of his life.

On the last day of last month died John Edward Stead, metallurgist and chemist. Throughout his career closely associated with the scientific development of the ferrous industries of this country, he had in 1901 received the Bessemer Medal of the Iron and Steel Institution. He had served that Institution as its President as lately as two years ago.

Thomas Pridgin Teale, of Leeds, died in his ninety-third year on the 12th of the present month. Distinguished as a surgeon he had contributed to the old established renown of Leeds as a school of surgery. His father before him was a Fellow of the Society. Eminent in the actual practice of his profession, he was also well known for inventions and writings regarding practical hygiene, and for his services to the cause of medical education.

At the Anniversary Meeting it cannot be out of place to iterate the main object of the Society's foundation—"the Improvement of Natural Knowledge," by discovery, and as a never-failing means to that end, the furthering of research. A reference made to it at last year's Anniversary dealt particularly with the funds at the disposal of the Society for assisting that great purpose. To-day, in reviewing, however briefly, the events of the past year, the Society recalls with lively gratitude the noble gift received from one of its Fellows, Sir Alfred Yarrow. It is a gift specially directed towards this same essential aim of the Society's existence. The Society is happy to have enlisted the services of Sir Alfred himself as a member of the Committee of Management of the Fund furnished by his generosity. The terms of his letter accompanying the donation were no less generous and public spirited than the gift itself. The letter is before you in the Report of Council, but let me quote one point from its contents, a suggestion of practical guidance, perhaps specially germane to a line of policy which began to shape itself in the Society last year, and in which this year has seen further progress. The letter stressed "that the money be used to aid scientific workers by adequate payment and by the supply of apparatus or other facilities, rather than to erect costly buildings."

The receipt of this splendid gift was followed at no long interval by the accruing to the Society of the valuable bequest from its past Fellow, the late Dr. Ludwig Mond. The accession of these funds to the means at the Society's disposal for advancing research has enabled, and suggested, systematisation of its provision for that end. Consideration was undertaken of some adjusted scheme whereby the disbursements the Society could hope to make for the furthering of research should keep suitably in sight the whole ambit of the Society's purview of natural knowledge, thus making for advance over a wide scientific front. For such a plan the Foulerton, Messel, Yarrow and Mond Funds, to mention them in their historical sequence, taken in conjunction and following the wishes of their individual donors, lend themselves well. The scope of destination of these Funds extends from Physics, Chemistry and Engineering, on the one hand, through Biology, to, on the other hand, "Medicine and such sciences as are connected with the discovery of the causes of disease and the relief of human suffering." The mere scant enumeration of the circle of the Natural Sciences suffices to show them as a band of brothers, and seeing them as such is to remember their call is for research, and not even solely for Science's sake itself, but for that of humanity as well.

And, in addition to the question of the breadth of field there remained that also of the particular form which help for research might take in order to be best effective in whatever field rendered. The consideration given to this has been very full and careful. It will be recalled that from the Donation Fund and from some other funds of smaller amount, and also through the Committee administering the annual Government Grant, the Society is able annually to make disbursements, helpful for apparatus and material, in response to applications in regard to particular items of research. Moreover, the Society has of Research Studentships five in addition to the Sorby Fellowship. All and each of these have rendered and are rendering valuable aid to scientific research in their several respective ways. Broadly taken, their destination is to workers of promise in the earlier period of their career; and such workers are thus provided with opportunity for proving the powers of their promise.

This year, in addition to the above, a generous and public-spirited step taken by the Worshipful Armourers' and Brasiers' Company enables the Society to participate responsibly in the management of yet another endowment of somewhat similar scope. Bearing in mind this relatively satisfactory provision already existent for these needs and recognising, further, the far-reaching outside provision available from Governmental and a number of public and private beneficiary sources, to meet requirements of a similar kind, the opinion arrived at after thorough consideration has been that a form of help specially called for, and specially likely to be effective in advancing discovery, would lie in the creation of greater opportunity for fully experienced investigators of already proven first-rate capacity in research. It is felt that increase of opportunity afforded to such investigators is likely to attain, with a prospect of comparative certainty, its recompense in the achievements such investigators will accomplish. To open up facilities for this class of investigator would seem particularly the province of the Society, and one in which its help could pursue required directions with especially whole-hearted conviction, because the Society in virtue of its own organisation has special opportunity for cognisance of the powers and scientific circumstances of representatives of this class of investigator. Over an ample field, and at many points in that field, the Society lives in contact with their endeavours, conversant with work they have already done and often with work they are, in fact, prosecuting, and could prosecute more fully had they increased opportunity for so doing. The desirability for encouragement of research from the Society to take this kind of shape seems enhanced by circumstances of the present time, including as this present time does the likelihood of an immediate future which will be one of anxiety for finding ways and means. In Institutions, University or other, for the most part such investigators occupy positions to which their opportunities for research attach rather as a secondary adjunct to calls of other nature upon their strength and time. Under an institution's financial stress the demand made by it upon members of its staff who have multifold duties other than research, is likely to be increased in directions away from research. This is a situation of hardship to the investigator and of detriment and mischance to the due advance of science itself.

Institutions, whether University or other, which are seats of learning, show themselves, in instance after instance, desirous for their personnel to prosecute research, but also, in instance after instance, embarrassed to secure to them adequate time for doing so. And yet the research activity of these men—or, for that matter, women—is a main source of that improvement of natural knowledge which it is the Society's great business to promote. A spring of indispensable supply for the production of new knowledge is thus stemmed or curtailed. Therefore, it is felt that the Society by securing, in co-operation with this or that particular institution, ample freedom of time for a distinguished member of the personnel there to undividedly prosecute research, may extend a form of help toward the advance of discovery particularly desirable and welcome. It is felt that by so doing the Society can gear most usefully its own motive help into the general existent running machinery for the production of new scientific knowledge. The hope is, and the belief is, that its action may thus provide exactly à something which other Institutions might have special difficulty in providing. The action it is taking marks a course which, although entered upon tentatively and to be judged finally by experience, is yet inaugurated with the foundation of three research Professorships of the Society. The regulations for these appointments have been drawn up with intention to give the Professors utmost freedom to carry out research in the way dictated by their individual attainment, temperament and inclination. Council have not thought fit to insist that the Professors either shall teach or shall not teach ; the sole restriction laid down is that to research shall their main energies be devoted.

At the Anniversary Meeting last year I had the pleasure of referring to the appointment, then literally hardly more than one hour old, of Prof. Starling as Foulerton Professor. This year has seen him Harveian Orator of the Royal College of Physicians and, as regards the Society, entered fully upon the actual activities of the Foulerton Professorship. Now, at this present Anniversary, the pleasurable privilege falls to me of announcing the appointments of Prof. Fowler and Mr. G. I. Taylor to the Yarrow Professorships. I may be allowed here a few words of reference to them. I follow the alphabetical order of their names. Prof. Fowler is known the world over as a spectroscopist whose researches have been of the greatest value to astronomy, to physics, and to chemistry. Entering on science first as a pupil of, and then as an assistant to, Sir Norman Lockyer, his earlier researches were, as that provenance made natural, astrophysical in kind, although the special technique which he developed was a technique of methods purely laboratory. He achieved extraordinary success in identifying lines observed in stellar spectra with lines which he was able to reproduce in the laboratory. He was able thus to assign the lines to their chemical origin; for instance, the origin of the bands which dominated the spectra of what were then described as stars of Secchi's third class had been a mystery for many years. Fowler was able to show that they were due to titanium oxide. He accounted for many of the bands in the sun-spot spectrum by showing that they belonged to "magnesium hydride." Again, he made an interesting study of the spectra of comets. The spectrum of the head had been observed by Donati in 1864 and had been fully studied by Huggins and others. It remained for Prof. Fowler to make a study of the tail spectrum of comets. He noticed first that the observed spectrum coincided with one which had been obtained in the laboratory arising from an impurity in low-pressure hydrogen. Finally, after much effort and laborious work, this spectrum was found to originate in carbon monoxide.

While these are perhaps some of the more striking of Prof. Fowler's successes in the region of astrophysics, he has also done a great deal of highly useful work in adding to our knowledge of the spectra of known terrestrial substances. Special mention may perhaps be made of his study of the spectrum of scandium, which proved to be important both in solar prominences and in sun-spots; of magnesium, in which he discovered new series of spectral lines; of strontium, in which he added several lines to the already known triple series; and of the active modification of nitrogen discovered by the present Lord Rayleigh.

At the time that these investigations were carried out there was no reason to suppose an immediate future of practical importance for the results obtained, but with the advent of Bohr's theory of atomic structure they have been found to provide exactly the material required for full discussion of the new theories of atomic structure, and for the acquisition of new positive knowledge as to the details of atomic mechanism.

Perhaps his success of most striking general appeal has been his direct experimental proof that the so-called ζ-Puppis series of hydrogen originate from helium and not from hydrogen at all. This result incidentally provided a striking confirmation of Bohr's theory of the origin of spectra.

In this field of research Prof. Fowler stands unrivalled. Recently he has been examining the changes which take place in the spectra of elements as one electron after another is removed; the results obtained are of fundamental importance. His last paper on the "Spectrum of Trebly Ionised Silicon" will still be fresh in the minds of many of our Fellows.

Branches of physical science other than those benefiting by Prof. Fowler's work have formed the field of research of the Society's other Yarrow Professor, Mr. G. I. Taylor, namely, mathematics, engineering and geophysics. Prof. Taylor started his scientific life as an applied mathematician, and the Society is still fortunate in receiving from him frequent mathematical papers on hydrodynamical themes. Before the advent of Mr. Taylor to this field it was almost a foregone conclusion that the results of mathematical research in a large part of hydrodynamics would not be confirmed by experiments; Mr. Taylor has opened an era in which experiments and analysis give confirmatory results. From abstract hydrodynamics he was led to research in practical problems of geophysics and meteorology. He has a distinguished record in aeronautical science, dating from the time when, acting as Meteorological Adviser to the Air Force, he was led to study the motions of the air, the causes and effects of eddies and the complicated phenomena to which these give rise. The application of much of his work to problems connected with aircraft is very direct. As the result of mathematical calculations he designed a parachute possessing many advantages in practice; quite recently he has published an important theoretical investigation as to the manner in which the forces on a model aeroplane in a wind-channel are affected by the eddies set up at the channel's mouth. Some contributions by him have proved of high value to the theory of the propeller.

He has been equally successful in the application of mathematics to engineering problems. In collaboration with Mr. A. A. Griffiths, he made use of the fact that the equations which determine the torsion of an elastic bar are identical with those representing the displacement of a thin membrane stretched over a hole of suitable shape when slightly distorted by uniform pressure. By micrometric measurements of the distortion of such a membrane he was able to deduce the torsion stresses inside a bar of specified cross-section, a procedure having practical applications of the greatest importance.

In the last Bakerian Lecture delivered before the Society, Mr. Taylor, in conjunction with Miss Elam, studied the strains in a single crystal of aluminium when stretched to breaking point, using a most ingenious combination of micrometric measurements and X-ray analysis. In this way he was able to trace the internal motions in the crystal and to explain the striking difference between the fracture of a bar of ordinary metal and that of a single crystal, such as he examined. In this, his most recent work, he has opened up a field which promises to be of far-reaching importance to the science of the strength of materials, and, I venture to think, of great practical value to the working engineer.

The record of both of our new Professors gives every justification for hoping that in the unfettered freedom of the Yarrow Professorships they may find the opportunity for still ampler fulfilment of brilliant work. It is fortunate that they will both continue their researches in the Laboratories from which their outstanding work has issued in the past, and of whose tradition indeed their reputations already are a part.

It is interesting for us to recall that to encourage and enable investigation in this kind of way has been, although only now entering within the Society's power of accomplishment, a near wish of the Society at past times in its history. These Professorships and the policy they indicate are reminiscent of a page of the very preface of the Society's whole story. If we turn to Bishop Sprat's contemporary account of the first years of the Society we see in that volume's frontispiece, freshly with us from Sir Robert Hadfield's recent admirable reproduction of it, the figure of Francis Bacon, along with those of the giver of our Charter, King Charles, and of the first President, Lord Brouncker. Sprat records that to Bacon's "New Atlantis" much of the inspiration for the inception and early life of the Society was due. The book had appeared some thirty-five years before the date of our first Charter. In it Bacon had outlined what to many seemed a sort of prototype foreshadowing the Royal Society itself: "a College," his words run, "for the obtaining of knowledge of the causes of things." He described that College's prospective grounds and apartments, and then enumerated its Fellows and their functions.

"Of its Fellows," wrote Bacon, "twelve there be that sail into foreign countries to bring patterns of experiments from all other parts. These we call merchants of light. Then three we have that collect the experiments which are in all books. These we call depredators" . . . "And," he continued, "on our foundation we have three Fellows who all their days try new experiments such as themselves think good. These we call pioneers." To-day, on the completion of its two hundred and sixty-first year of existence, the Society finds itself able to fulfil, and is fulfilling, closely this particular of Bacon's enthusiastic imagining. Three Fellows on its Foundation to "try all their days new experiments such as themselves think good." Like Lord Bacon we may well designate them pioneers. And also we shall think of them as Yarrow Professor Alfred Fowler, Foulerton Professor Ernest Starling, and Yarrow Professor G. I. Taylor. Let me add how earnestly we wish them all success in their "new experiments such as themselves think good."

And, finally, may I in general terms return once more to summarise that leading motive, which has actuated the launching of these new Professorships. Our Universities and other scientific institutions have been wont, indeed in many cases by force of circumstances are compelled, to regard teaching as the primary occupation of Professoriate and Staff, and to envisage their occupation in research as merely secondary to their occupation in routine teaching. The Society has inverted quite deliberately that order of precedence of professorial function. By this inversion the Society of set purpose desires to recognise research as a definite profession and to advance, and to maintain, the principle that the labourer is worthy of his hire no less when engaged in research than when engaged in class instruction.

And upon this subject yet one word more. Munificent as the gifts are which the Society has received, enabling it to do what it is doing toward this end it has at heart, may we not venture to hope that the funds already to hand for that purpose will prove but the auspicious starting-point for yet others of similar destination. To say this is but to echo the concluding sentence of Sir Alfred Yarrow's memorable letter. With such aspirations, our desire is that in due course either the Royal Society or other bodies may have it in their power to endow the research of all those individuals whose life ought, in the best interests of the Community, to be devoted to scientific research as the main purpose of their life-career.

Last year, allowing myself a reference to physiology and its progress, I adverted to the high promise for importance implied in the discovery of "insulin" by Drs. Banting and Best in Prof. J. R. Macleod's laboratory at the University of Toronto. Professor Macleod was among the candidates elected to the Fellowship of the Society this spring. Insulin's promise of fruitfulness has in the elapsed twelve months proceeded satisfactorily toward further fulfilment. It would seem prospectively possible that under treatment by insulin the β-cells of the pancreatic islets may be able to re-establish permanently their functional powers, and that in certain cases the treatment may produce not only temporary but lasting relief from the diseased condition. All the more welcome therefore is it to note that international recognition of their work was last month received by Dr. Banting and Professor Macleod in the form of the award of the Nobel Prize for Medicine for 1922. The success of their work was based on intimate co-operation between physiology and biochemistry—if, indeed, these cognate studies can be considered separate—and the success of their research early in its progress instanced the value of team-work in the best sense of that term. That aspect of it cannot be touched without a word of tribute to the act of comradery on the part of the two Nobel Laureates themselves in sharing their emoluments from that prize with their two other collaborators, Dr. Best and Professor Collip. And exemplifying the admirable furtherance of a scientific enquiry by organised collaboration, on a wider scale, yet tantamount in fact to team-work, has been the rapid advance made for the year in the whole study, practical and theoretical, of insulin and insulin-treatment under the earnestness and wisely-directed energy of the Medical Research Council.

And, leaving insulin to its success, let me turn finally to mention of a further richly deserved international recognition won by the work of another Fellow of our Fellowship, Professor A. V. Hill, of University College, London. The award to him of the Nobel Prize in Medicine is specially and universally gratifying to physiologists. His investigations have dealt with the thermodynamical processes underlying muscular contraction, and underlying also the muscular restoration after contraction, enabling contraction to repeat itself again. Professor Hill's elucidation of this whole problem, one which has long occupied and taxed the powers of many eminent physiologists, is as far-reaching in outlook as it has been masterly in conception and in execution.

I now proceed to the presentation of the Medals. The Copley Medal is awarded to Prof. Horace Lamb.

For forty years Professor Lamb has been recognised as one of the most prominent and successful workers in applied mathematics in this country. He is the foremost authority on hydrodynamics, not only in this country but the world over. His treatise on this subject, now in its 4th edition, has long been the standard textbook. Its first edition systematised for the first time the science of hydrodynamics as that emerged from the researches of Stokes, Kelvin and others. With successive editions the book has increased in range and size, and included more and more of the author's own researches, until it finally takes rank among the classical treatises in the domain of mathematical physics.

Professor Lamb's scientific activity, originally centring around the subject of hydrodynamics, has radiated thence into most branches of physical science. His earlier papers were concerned largely with investigations of solutions of the wave-equation

$$\nabla^2\phi = \frac{1}{V^2}\frac{d^2\phi}{dt^2},$$

especially with reference to spherical boundaries; they have exercised much influence on developments regarding elasticity and electricity, as well as hydrodynamics. The directness and elegance of his mathematical investigations are no less conspicuous than is their close contact with actual phenomena. His work contains much that is typical of the best qualities of British Applied Mathematics. He may be regarded as the outstanding representative to-day of the school founded by Stokes, Kelvin, Clerk-Maxwell, and Rayleigh.

In recent years he has made important contributions to seismology, the theory of tides, and other branches of geophysics. The breadth of his scientific knowledge, along with the soundness of his judgment and clearness of his vision, have made him a highly valued member of many technical Committees both during the war and subsequently. Specially perhaps should be mentioned the assistance he has given of recent years to the Aeronautical Research Committee. Mathematical questions involved in the flow of air round aircraft, in the action of propellers, and the stresses in aeroplane structure, are of fundamental importance, but are exceedingly difficult; and here, as elsewhere, Professor Lamb's mathematical skill and power of clear exposition have proved of the highest value. By his personal qualities no less than by his outstanding powers as a teacher and investigator he has, for all in contact with him, been a great influence.

A Royal Medal is awarded to Prof. Charles James Martin.

Professor Martin is distinguished for contributions both to physiology and to pathology. Investigating snake venoms he differentiated two groups in virtue of their action, one nervous, the other, so to say, humoral. His work on heat-regulation in monotremes threw light on the evolution of the thermotaxis of warm-blood animals. More recently his researches have lain in the colloidal chemistry of proteins, and in protein-metabolism. A series of experiments carried out by him in collaboration with his colleague, Mr. Robison, on the minimum nitrogen expenditure of man and the biological values of separate kinds of protein-food stands as one of the most valuable contributions yet made to a subject as difficult as it is important. Besides these personal researches at first-hand, Professor Martin has influenced inspiringly the course of research in medicine in this country. He was a member of the Plague Commission which organised the researches finally determining the mode of transmission of that disease. He was Chairman of the War Office Committee on Anti-typhoid Inoculation. As Director of the Lister Institute he has contributed to many investigations, in addition to those actually issued in his name. Thus he has been intimately associated with the enquiry into the influence of accessory food factors of diet in the prevention and remedying of "deficiency" diseases, such as scurvy and rickets, an enquiry the success of which may be regarded as one of the recent triumphs of preventive medicine. His abilities have been ever at the call of his colleagues, and in the most public-spirited way devoted to the service of the community in general.

A Royal Medal is awarded to Sir William Napier Shaw.

In the great advances made during the last twenty-five years in the science of meteorology, Sir Napier Shaw has been amongst the foremost pioneers. During his twenty years' administration at the Meteorological Office that Office saw three marked steps forward: two of these have been changes in its quarters; the third and greatest has been the change in outlook of the work of the Office, whereby it assumed, under Sir Napier Shaw's stimulating influence, the character of a scientific institution for the interpretation of meteorological phenomena. With the assistance of his scientific staff, he has developed the physical and dynamical aspects of the subject, and has done much to concentrate attention upon the thermodynamics of meteorology, wherein the motions of the water-laden air are interpreted as the action of a thermodynamic engine. By his personal researches and especially in his capacity as President of the International Meteorological Committee he has rendered great services to all branches of the science. He has encouraged the co-ordination of international effort in the study of the meteorology of the globe. He has emphasised the need for systematic treatment of the phenomena in terms of units, in line with the established methods of physics and thermodynamics. His contributions to knowledge of the air and its ways have been largely responsible for changing the basis of meteorology from one of empiricism to one of science. I may mention his investigation of the "Life History of Surface Air Currents," which changed completely the conception of the motion of air in cyclones and anticyclones; his pioneer study of the effect of weather on crops; and his more recent work on the general circulation of the atmosphere which has introduced the notion of an atmosphere largely rigid to vertical motion and the importance of applying thermodynamical considerations to the atmosphere treated as a whole.

The Davy Medal has been awarded to Prof. Herbert Brereton Baker.

Prof. Baker's researches in various fields of chemical investigation, his examination of highly purified tellurium from various sources for the possible presence of higher members of the same group of elements, and the redetermination of its atomic weight, are of outstanding merit. It is, however, his remarkable researches on the influence of traces of water in modifying chemical change, whether of the nature of combination or of decomposition, which constitute perhaps his especial distinction. For the last forty years he has carried on continuously a series of experiments characterised throughout by extreme insight, patience and manipulative skill. The results obtained by complete drying were as remarkable as they were unexpected, because they were in direct opposition to those which followed careful drying by usual methods. For example, he showed that ammonia and hydrogen chloride could be dried so thoroughly that they would not combine, and that ammonium chloride, when completely dried, could be vaporised without dissociating into its constituents. Still more striking was the demonstration that silver could be fused in an atmosphere of pure, dry hydrogen and oxygen without explosion, though explosion followed instantly upon the admission of a trace of water vapour.

The bearing of Prof. Baker's researches on theories of chemical change is as important as his conclusive experimental demonstrations of the phenomena themselves.

The Hughes Medal is awarded to Dr. Robert Andrews Millikan.

Dr. Millikan has long been regarded as one of the most skilful experimenters in physical science. He is awarded the Hughes Medal especially for his determinations of the electronic charge e and of Planck's constant h. When physicists were still ignorant of the value of the electronic charge to within 5 per cent., Dr. Millikan, by a method of the utmost ingenuity, arrived at the value $4 \cdot 774 \times 10^{-10}$ E.S.U., for which he claimed an accuracy of one part in a thousand, a claim which has stood the test of time. His determination of *h* was not only remarkable in itself, but was of still greater value as finally vindicating the Einstein-Bohr view of the nature of the photo-electric phenomenon.

The Structure of Aragonite.

By W. L. Bragg, F.R.S., Langworthy Professor of Physics, Manchester University.

(Received November 27, 1923.)

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1. Aragonite has the same composition as calcite, both being crystalline forms of calcium carbonate, $CaCO_3$. A comparison of the structures of these two crystals is interesting, because they represent one of the most striking cases of dimorphism amongst minerals. Calcite forms rhombohedral crystals, whose structure has been analysed by several workers.[*][†][‡] Aragonite crystals[§] have orthorhombic symmetry, and are generally assigned to the holosymmetric class. According to Miers (Mineralogy, Part II, Section XIV) etching experiments indicate that the symmetry may really be polar. The analysis which is described below places aragonite in the holosymmetric class of the orthorhombic system, and though it is always possible that the actual

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[*] W. L. Bragg, 'Proc. Roy. Soc.,' A, vol. 89 (1913).

[†] W. H. Bragg, 'Phil. Trans. Roy. Soc.,' A, vol. 215 (1915).

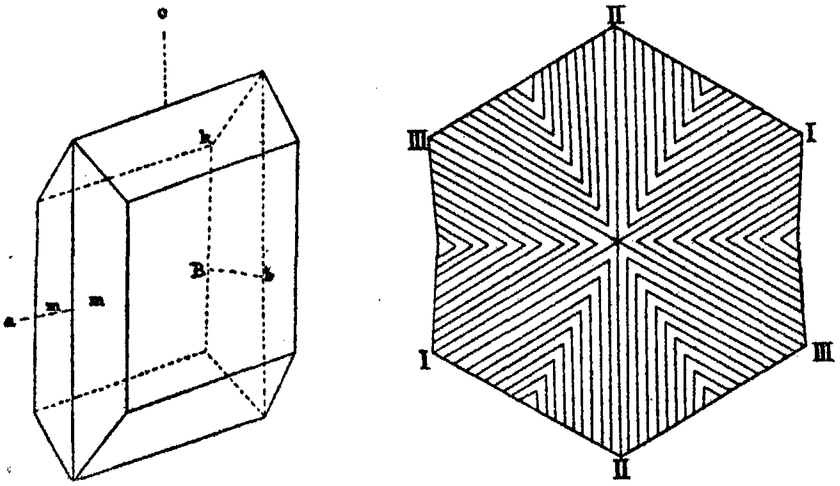
[‡] R. G. Wyckoff, 'Am. Journ. Sci.,' vol. 50 (Nov., 1920).

[§] A structure for aragonite has been proposed by M. L. Huggins ('Phys. Rev.,' vol. 2, p. 19, 1922) which is based on considerations of electron arrangement. An X-ray examination shows that this structure is not the true one, as its fundamental spacings are incorrect.

structure may have a lower symmetry owing to some distortion which is not revealed by X-ray examination, it would appear that this distortion is very small.

Crystals of aragonite have an obviously pseudohexagonal character. This is revealed by the axial ratios, by the common forms of the crystals, and by their twinning. The '*c*' axis is the pseudohexagonal axis. The faces (010), (110), marked 'B' and '*m*' in fig. 1A, build up a form which is very nearly hexagonal, the angle $(\bar{1}10):(110)$ being 63° 48′ instead of the 60° required by hexagonal symmetry. Simple crystals are rare, as twinning about the plane (110) is nearly always present. Repeated twinning about this plane results in interpenetrating groups which are almost indistinguishable from simple hexagonal crystals (fig. 1B).

The structures of calcite and aragonite are typical of many other forms.



A. B{010} *m*{110} *k*{011}

B. Triplet twinned on (110).

FIG. 1.—Aragonite.

The carbonates of magnesium, manganese, iron, zinc, and cadmium are isomorphous with calcite, as is also the double carbonate of calcium and magnesium (dolomite), while the carbonates of strontium, barium and lead are isomorphous with aragonite. The nitrates of sodium and potassium are in an interesting relationship to these carbonates. Sodium nitrate is built up in the same way as calcite, whereas potassium nitrate in its stable form has the aragonite structure. Potassium nitrate is stated to pass over into a rhombohedral modification resembling calcite at high temperatures.

2. If the pseudohexagonal outward character of the crystal is an index

to the underlying structure, pairs of planes such as 'B' (100) and '*m*' (110) should give similar X-ray reflections. This is actually the case, as a glance at fig. 2 will show. For both planes the spectra occur at nearly the same angles, and have the same characteristics. The first-order spectrum is too small to observe, the third order is large compared with the second order; fourth and sixth order spectra are strong, whereas the fifth order is very small. The planes (100), (130) form a similar series. The face (100) would cut off the edge between '*m*' and '*m*' in fig. 1, and the face (130) the edge between '*m*' and 'B.' If the crystal were hexagonal, these faces would be identical in all respects. In aragonite, they yield spectra at almost the same angles, first and second orders being strong and the third and fourth orders weak.

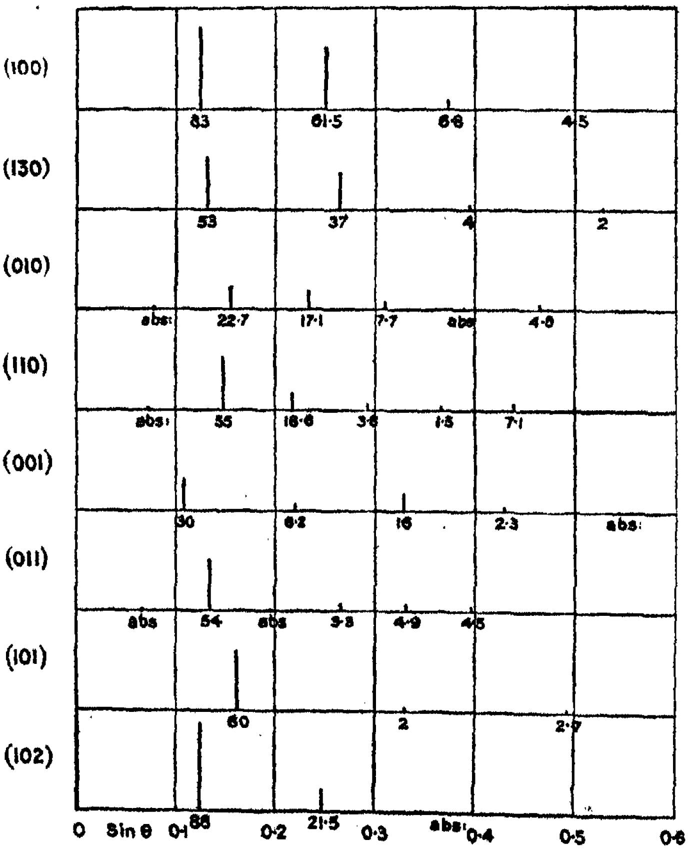


FIG. 2.—Reflexion of the rhodium K_a doublet by aragonite. Figure beneath each peak denotes intensity of reflexion as percentage of reflexion (200) NaCl.

The reflections of the rhodium K_a doublet from a number of faces are plotted in fig. 2. The intensity of the reflection was measured in each case by the method first used by W. H. Bragg,* the crystal being moved through the reflecting position at a constant rate and the integrated reflection observed. In the figure, the intensity is plotted as ordinate, and the sine of the glancing angle as abscissa. These intensities could not, in all cases, be checked by measurements made on several specimens, since untwinned crystals on which faces can be cut are hard to obtain. When such a check was made, results sometimes varied by 10 or 15 per cent. For the purpose of analysis, however, a survey which gives the approximate relative intensity of the reflections for a large number of faces, is of more value than a very accurate measurement of these intensities for a few faces. We are still in so much doubt as to the laws which govern the intensity of reflexion of a crystal that we are not in a position to utilize to the full the accurate measurements of intensity which can be made. In all cases, the second order reflexion from the cube face of rocksalt (ground face) was used as a standard, and other intensities are expressed as percentages of this effect.

3. P. Groth ('Chemische Krystallographie') assigns to aragonite a density between 2·926 and 2·933, and axial ratios $a : b : c = 0\cdot6228 : 1 : 0\cdot7204$. The first-order X-ray spectra give the following data :—

$$d_{(100)} = 2\cdot47\ \text{Å},\ d_{(010)} = 3\cdot97\ \text{Å},\ d_{(001)} = 2\cdot86\ \text{Å}.$$

These quantities are in the same ratio as a, b, and c, and calculation shows that a volume equal to $2d_{(100)} \times 2d_{(010)} \times 2d_{(001)}$ contains four molecules of $CaCO_3$. The observed angles of reflexion do not differ by more than a few minutes of arc from those calculated with the density and axial ratios given above, and I have not attempted to correct these data by making a very accurate determination of the crystal spacings. The structure which will be described is based on a simple orthorhombic lattice, the primitive translations of which are $2d_{(100)}$, $2d_{(010)}$, $2d_{(001)}$. These translations will be designated below by $2a$, $2b$, $2c$. Although it is not possible to define uniquely the $CaCO_3$ molecule in the crystal, groups of this composition can be so chosen that they lie on four interpenetrating simple orthorhombic lattices.

In making a first approximation to the general marshalling of the atoms in aragonite, we may be guided by the considerations that the structure has pseudo-hexagonal symmetry, and that the unit orthorhombic cell contains four molecules. The calcium atoms and CO_3 groups must lie close to positions which would correspond to a holosymmetric* hexagonal structure, since the spectra from pairs of faces such as ' B ' and ' *m* ' are so alike. This approximation to a structure of high symmetry reduces the number of possible arrangements to very few, which can be tried in turn to see whether they are in agreement with the broad features of the spectra. If we consider the CO_3 group as a simple unit, disregarding for the present purpose the question of its orientation and internal structure, a trial of the various possibilities makes it clear that the only arrangement of Ca atoms and CO_3 groups which satisfies the necessary conditions is based on the hexagonal close-packed assemblage.

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* W. H. Bragg, 'Phil. Mag.,' p. 881 (May, 1914).

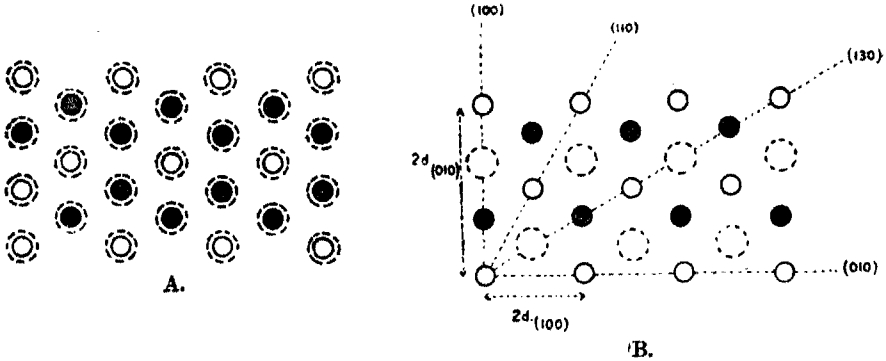

Fig. 3.—Marshalling of Calcite (A) and Aragonite (B).

The small circles indicate the positions of the calcium atom, the dotted circles the positions of the CO_3 groups. Atoms similarly shaded lie on the same layer.

Fig. 3 illustrates the cubic and hexagonal close-packed arrangements projected on a plane perpendicular to a trigonal axis, and to the hexagonal axis, respectively. In both systems the layers consist of atoms arranged at the corners of equilateral triangles. Starting with one such layer, the next is arranged so that its atoms fall over the centre of the triangles in the layer below. In the cubic system the third layer lies over centres of triangles in both the first and second layers, and the structure is not repeated till the fourth layer is reached, whereas in the hexagonal system the third layer lies directly over the first.

If the hexagonal close-packed assemblage is referred to a set of orthorhombic axes, the ' *c* ' axis being parallel to the hexagonal axis and the ' *a* ' and ' *b* ' axes having the directions marked in fig. 3 (B), it will be seen that the (010) and (110) planes have the same spacing and arrangement, and that this is greater than the spacing of the (100) and (130) planes, which are also alike, in the ratio $\sqrt{3} : 1$. This closely approximates to the ratio of the spacings of these planes in aragonite. Further, the peculiar structure of the (010) and (110) planes, where the reflected wave is the resultant of two components with a phase difference of $2\pi/3$ for the first order, leads to large third and sixth orders, such as are observed in the corresponding aragonite spectra. The orthorhombic cell whose sides are $2d_{(100)}$, $2d_{(010)}$, $2d_{(001)}$ contains four representative points, the number required for the aragonite structure.

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* It is holosymmetric because the structure has symmetry about three planes at right angles to each other.

The structure of calcite may be regarded as based on a cubic close-packed point system, which has been compressed along a trigonal axis until the three rhomb edges meeting in this axis make an angle of 101° 55′ with each other instead of 90°. The calcium atoms and CO_3 groups are marshalled in the way indicated in fig. 3 (A). In aragonite it will be shown that the calcium atoms lie very near to the positions indicated in fig. 3 (B). There is a close parallelism between the two structures. The distance, measured perpendicularly to the plane of the diagram, between successive layers of calcium atoms, is 2·86 Å (d_{111}) in calcite and 2·86 Å (d_{001}) in aragonite. The distance between calcium atoms lying in the same layer is 4·96 Å in calcite. In aragonite the distance is slightly different for different directions, being 4·94 Å parallel to the '*a*' axis, and 4·66 Å in the other two directions. Aragonite is correspondingly denser than calcite, since the latter distances are rather smaller than the former.

In calcite the CO_3 groups lie midway between every pair of equilateral triangles of calcium atoms, which are in successive layers. In fig. 3 (A) the CO_3 groups which lie between the triangles of first and second layers will be below the calcium atoms of the third layer, and so on. Similar situations for the CO_3 groups can be found in aragonite, as fig. 3 (B) shows. In this case all the groups will be at the centres of the hexagonal cells in the projection. However these groups may be oriented, it can readily be calculated that their presence in this situation will nearly destroy the first order reflexion from the (010) and (110) planes, thus explaining a marked feature of the spectra in fig. 2, where this order is absent.

Other marshallings of the Ca atoms and CO_3 groups which have hexagonal symmetry and an equivalent number of molecules to the unit cell may be found. For instance, the Ca atoms and CO_3 groups of fig. 3 (B) may be interchanged. A trial of these other arrangements shows that they cannot explain the main features of the spectra and may therefore be ruled out.

4. Commencing with this structure, which has complete hexagonal symmetry when the CO_3 groups are regarded as single units, we will now consider what

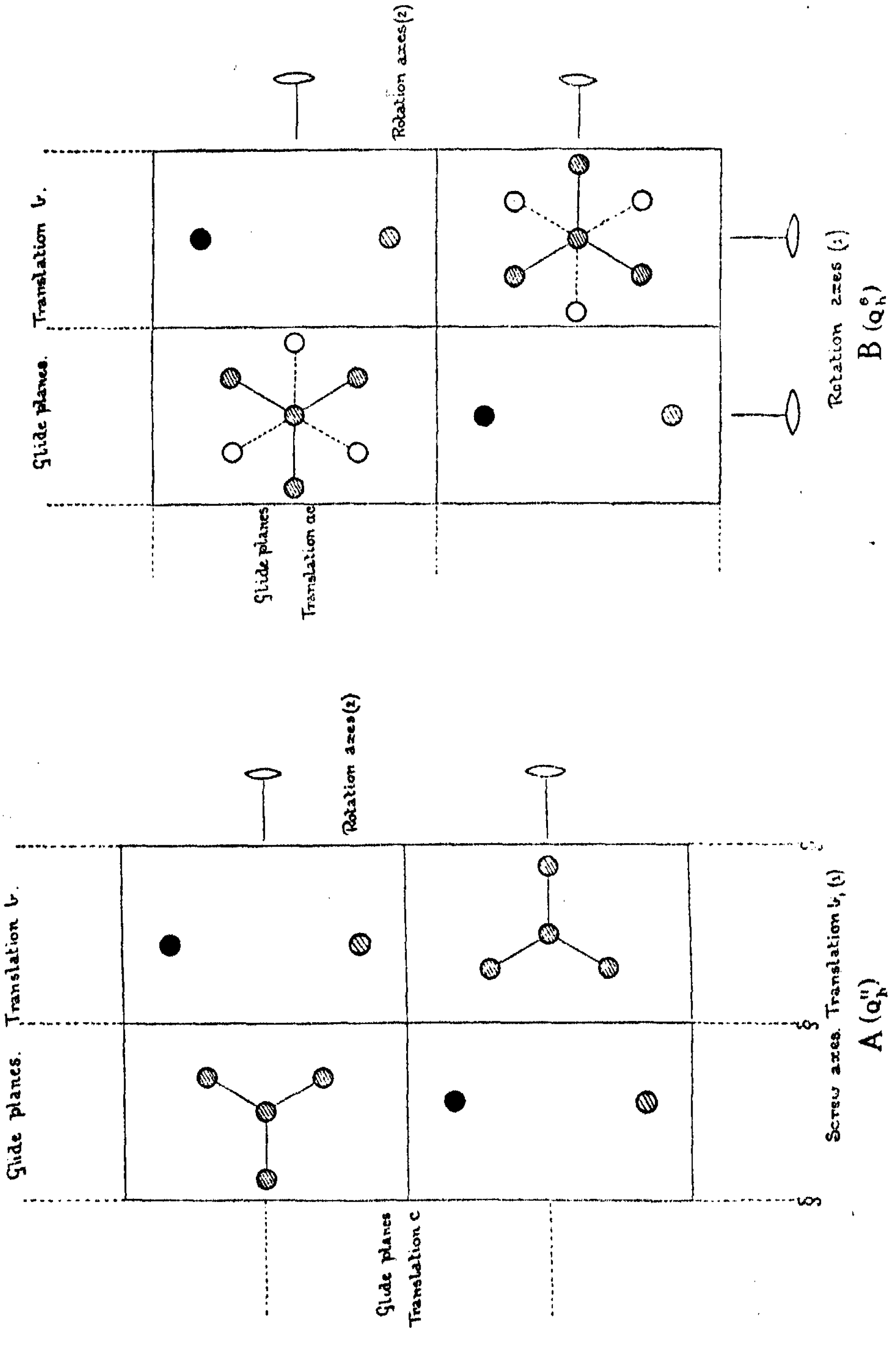

Rotation axes(2)
Translation b.
Glide planes.
Glide planes
Translation ac
Rotation axes (1)
B (q_h^6)
Rotation axes(2)
Translation b.
Glide planes.
Glide planes
Translation c
Screw axes. Translation b, (1)
A (q_h^{11})

FIG. 4.

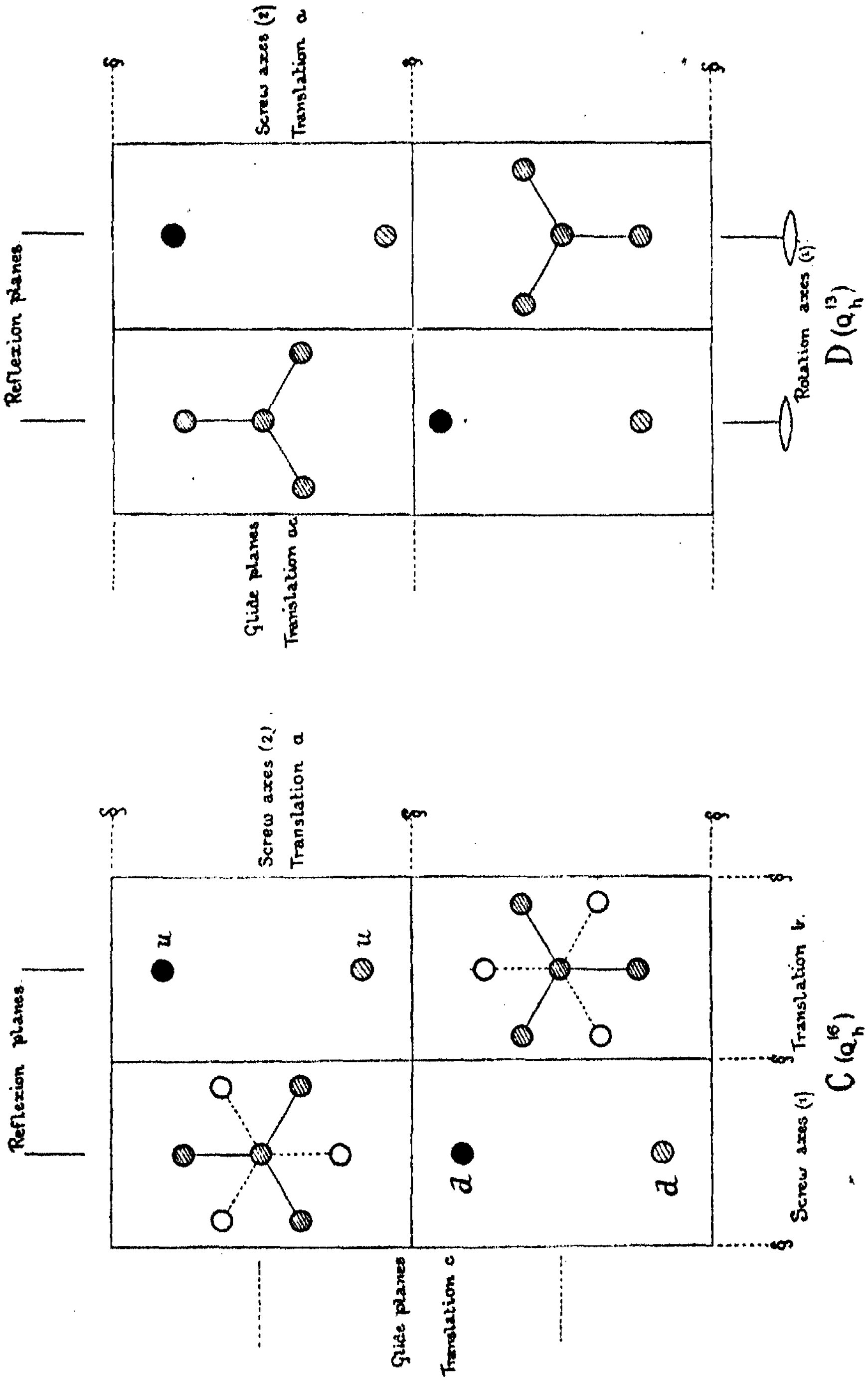

Reflexion planes
Screw axes (2)
Translation a
Glide planes
Translation ac
Rotation axes (1)
D (q_h^13)
Reflexion planes
Screw axes (2)
Translation a
u
u
d
d
Glide planes
Translation c
Screw axes (1)
Translation b
C (q_h^16)

FIG. 4.

deformations it can suffer while yet retaining sufficient elements of symmetry to build up a holohedral orthorhombic crystal.

Fig. 4 shows four ways in which these deformations may take place, each being based on a space group with distinctive elements of symmetry. The structure is projected on a plane perpendicular to the 'c' axis, as it is in fig. 3 (B). Planes of symmetry perpendicular to the plane of projection, and axes of symmetry parallel to this plane, are indicated in each case to show that the structures are holosymmetric. The other axis and plane of symmetry and the centre of symmetry are not marked, but their positions will be clear from the diagrams. The shading of the atoms indicates the level of the planes on which they lie, the most heavily shaded being uppermost.

These are not the only space groups on which the crystal structure may be built while still approximating to the hexagonal marshalling. The pseudo-hexagonal arrangement of fig. 3 has two types of centres of symmetry. These lie midway between the planes containing calcium atoms, at the corners and centres of the rectangles of fig. 4. A centre of symmetry cannot exist in the latter positions in aragonite, however, since the CO_3 group must lie near these positions and such a group cannot have symmetry about a centre. The symmetry condition could be satisfied by placing a pair of CO_3 groups in half the positions and none at the others. Such an association of the negative ions in pairs is unlikely from a physical point of view, and is not in accordance with the arrangement of CO_3 groups in fig. 3. All possible space-groups with a centre of symmetry of the other type are included in fig. 4.

One method of deciding which of these space groups forms the basis of the aragonite structure consists in calculating the fundamental spacings of a number of planes for each space group, and comparing these with the positions of the observed first-order spectra. Such a method involves no consideration of the intensities of the spectra. It has been used with conspicuous success by W. H. Bragg in analysing complex organic crystals, where intensities cannot be used to fix the exact positions of the atoms. By its help the space group on which the crystal is built can be found, and a knowledge of the approximate dimensions of the molecule leads to a close determination of the structure.

In the case of a crystal such as aragonite this method is, of course, just as decisive in distinguishing between the different space groups. It is not the only method, however, which can be used for this purpose. We can show that certain of the space groups would not only give incorrect positions for the first-order spectra, but would also be quite incapable of explaining the relative intensities of the higher orders. An examination of spectral intensities provides, therefore, as sure a criterion as an examination of fundamental spacings. All tests which can be applied agree in designating the space group (C) as being the correct one.

The spacings of the orthorhombic lattice whose translations are $2a$, $2b$, $2c$ may be taken as standard. They are compared with the spacings of the four groups in the following table :—

	A.	B.	C.	D.	Observed.
100	Normal	Halved	Halved	Halved	Halved.
010	Halved	Halved	Halved	Normal	Halved.
001	Halved	Halved	Halved	Halved	Halved.
011	Halved	Halved	Normal	Normal	Normal.
101	Halved	Normal	Halved	Normal	Halved.
110	Normal	Normal	Normal	Normal	Normal.
130	Normal	Normal	Normal	Normal	Normal.
102	Normal	Halved	Normal	Halved	Normal.

It will be seen that the group (C) is the only one which corresponds with observation. The conclusion that the crystal is built on the space group of fig. 4 (C) is also reached by a consideration of the orientation of the CO_3 groups. In space groups (A) and (B) the situations occupied by these groups are traversed by a digonal rotation axis. A single CO_3 group can satisfy the symmetry conditions if one oxygen atom and a carbon atom lie on the axis, and the other two oxygen atoms are placed so that the line joining them is bisected at right angles by the axis. CO_3 groups so arranged are shown in the diagram.

These two systems are definitely excluded by the spectra yielded by the (001) face of the crystal. In these systems the (001) planes have the following structure :—

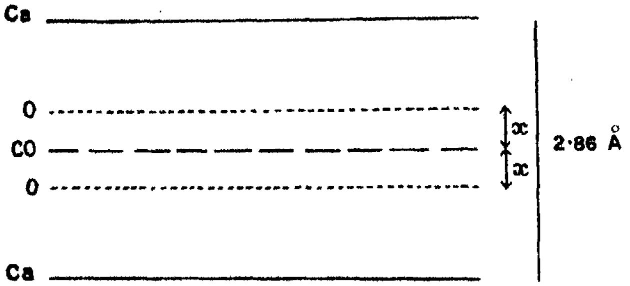


FIG. 5.

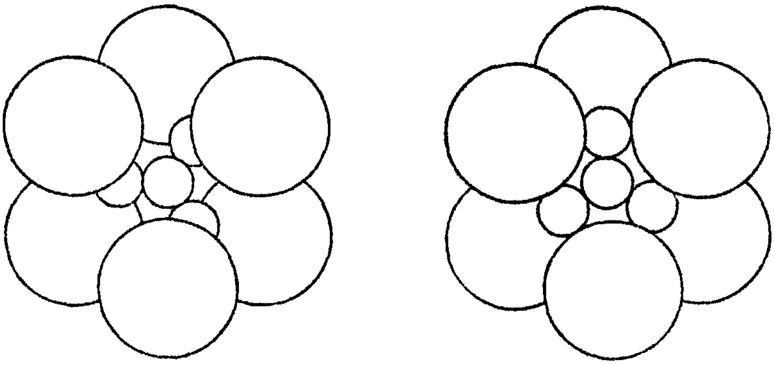
The Ca atoms lie on planes which have, half-way between them, planes containing one carbon and one oxygen of every CO_3 group. The parameter x depends on the positions of the other two oxygen atoms, and may have any value. The (001) spectra are characterised by a small first, second, fourth and fifth orders, and large third and sixth orders. *No value of x can possibly account for these features.*

In the systems of fig. 4 (C) and (D) the situation for the CO_3 group is traversed by a reflexion plane. One carbon and one oxygen must lie on this plane, and the other two oxygens must be mirror images of each other in it. In these systems the CO_3 group as a whole may be moved up or down parallel to the '*c*' axis, as may also the calcium atom in fig. 4 (C), and it is possible to find an arrangement which explains the (001) spectra. Symmetrical displacements of the Ca atoms are denoted by letters 'u' and 'd' in the diagram. It has already been seen that fig. 4 (D) is impossible because it gives the wrong fundamental spacings. In addition to this, the Ca atoms belong to two classes, atoms of the one class being differently situated to atoms of the other class. This is not impossible, but it is improbable, as it would be the first instance of such a division in crystal structures.

Finally, it will be shown below that a CO_3 group, *of the same dimensions as the CO_3 group in calcite,* oriented as in fig. 4 (C), will explain the relative intensities of all the spectra from the planes (100), (130), (010), (110), whereas a group oriented as in fig. 4 (A) and 4 (B) cannot be made to do so. We conclude that the CO_3 group is so oriented that it has symmetry about a plane parallel to the '*b*' and '*c*' axes of the crystal.

This orientation of the CO_3 group has an interesting physical significance. In calcite, each oxygen atom lies between two calcium atoms, in the position shown in fig. 6. In aragonite it must be supposed that the whole CO_3 group has turned round through 30°, so that each oxygen now lies between three calcium atoms. This suggests an explanation of the striking difference between the spectra of the (111) calcite and (001) aragonite planes, which are otherwise so similar in their structure and have an identical spacing. In calcite the CO_3 group lies exactly midway between the planes on which the calcium atoms lie, and in consequence the (111) planes have a structure Ca....CO_3....Ca which should yield a small first-order spectrum, a large second order, a small third order, and a large fourth order. This is found by experiment to be the case. In aragonite, if the oxygen atom is approximately equidistant from the three calcium atoms and so at the centre of a triangle, such as ABC in the figure, the whole group will be at a distance of $c/3$ from the AB plane.

Groups pointing in the reverse direction will be at a distance of $2c/3$ from this plane, and the planes will have a structure Ca . . . $CO_3/2$ . . . $CO_3/2$ . . . Ca.



A. Environment in Calcite. B. Environment in Aragonite.

FIG. 6.—CO_3 Group.

This would give a first, second, fourth and fifth order descending normally, and an abnormally large third and sixth order, and this is exactly what is observed.

5. The above argument as to the possible configurations of the aragonite structure may be expressed in the terms of mathematical crystallography, following the notation of Hilton,* which is based on that of Schonflies. Commencing with the hexagonal close-packed point system, this may be imagined to be distorted till its axial ratios correspond to those of aragonite. This is done by a large compression along the '*c*' axis and a slight compression along the '*b*' axis. It then consists of two intersecting orthorhombic lattices (Γ_0'), faces of the orthorhombic cell perpendicular to the '*c*' axis having points at the centres. It is based on the space group Q_h^{17}. There are both rotation and screw axes parallel to the '*a*' and '*b*' axes of the crystal, but only screw axes parallel to the '*c*' axis. The axes of symmetry form by themselves the space group Q^5. A consideration of the positions of first order spectra, and of the possible symmetry of the CO_3 groups, shows that all the elements of symmetry of Q_h^{17} cannot be retained, and that the structure is based on the orthorhombic space lattice (Γ_0). The axes of such a lattice must belong to the groups Q^1, Q^2, Q^3 or Q^4. Q^1 does not come into consideration, for it has rotation axes parallel to all the orthorhombic axes, whereas the complete group Q_h^{17}, built on the axes of the space group Q^5,

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* Hilton, 'Mathematical Crystallography,' pp. 192 *et seq.*

has only screw axes parallel to the '*c*' axis. Q^2, Q^3, Q^4 are all possible groups.

Q^2 has two rotation axes and one screw axis which meets both of the others. There is only one way of choosing this system from the complete group Q^5. Q^4 has three non-intersecting screw axes. There is again only one way of choosing such a system from the group Q^5. Q^3, on the other hand, can be formed from Q^5 in two ways. It contains one rotation axis and two screw axes, which intersect each other but do not meet the rotation axis. We thus have four possible ways of choosing a system of axes from the group Q^5, which will serve as basis for a structure built on the simple orthorhombic lattice (Γ_0). These groups must be combined with inversion about a centre of symmetry in order to arrive at a holohedral space group. In the distorted hexagonal structure, based on $Q_h{}^{17}$, there are two such centres. One is in the position which is to be occupied by the CO_3 groups, the other in the same plane (001) but half-way between neighbouring CO_3 groups. The first centre of symmetry cannot exist as it is incompatible with the symmetry of the CO_3 group. Combining the other centre of symmetry with the four systems of axes described above we get :—

$$(a)\ (Q^3, I_m) = Q_h{}^{11}.$$
$$(b)\ (Q^2, I_r) = Q_h{}^{6}.$$
$$(c)\ (Q^4, I_m) = Q_h{}^{16}.$$
$$(d)\ (Q^3, I_f) = Q_h{}^{15}.$$

The indices *m*, *r*, *f*, refer to the figure on p. 194 of Hilton's book. These are the four groups which have been considered above, (*c*) being chosen as the correct one.

The unit orthorhombic cell contains four CO_3 groups. Since the structure is holohedral with eight faces in the general form, each group must possess one element of symmetry. In (*a*) and (*b*) it has symmetry about an axis; in (*c*) and (*d*) symmetry about a plane. In all cases the symmetry is raised to the eight-fold type by the re-duplication of the CO_3 groups, according to the general rule to which attention has been drawn by W. H. Bragg* and Shearer.†

6. It will be assumed that the structure of aragonite is based on the system of symmetry represented by fig. 4 (C). In seeking to explain the observed spectra the atoms may be moved about in any manner consistent with this

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* W. H. Bragg, "The Significance of Crystal Structure," 'Trans. Chem. Soc.,' vol. 121, p. 2769 (1922).

† Shearer, 'Proc. Phys. Soc.,' vol. 35, Part 2, p. 81 (1923).

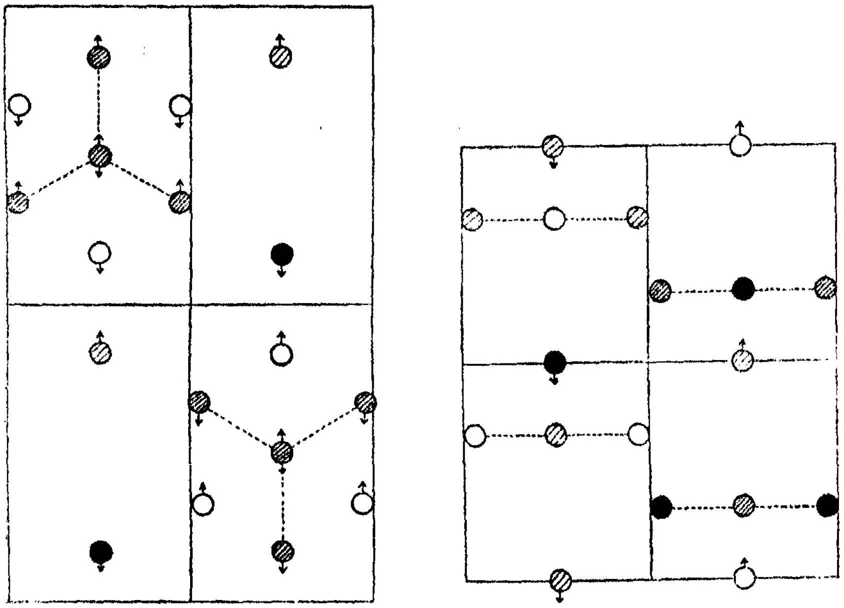
symmetry. The structure has nine parameters which must be evaluated. The calcium, carbon and unique oxygen atoms lie on symmetry planes, and so are fixed by two parameters each. One of the remaining oxygen atoms is the mirror image of the other, so three parameters fix these atoms, making a total of nine.

It will first be shown that an exceedingly simple arrangement of the calcium atoms and CO_3 groups explains the main features of each set of spectra tabulated in fig. 2. The correspondence is so close that the actual disposition of the atoms cannot differ greatly from this simple form ; however, a comparison of the spectra yielded by the different faces shows that this arrangement is not exactly right, and in the next paragraph the effect of distorting it will be analysed, in order to get a closer approximation to the actual structure, and to estimate the accuracy with which the nine parameters have been determined.

In fig. 7 the unit orthorhombic cell, containing four $CaCO_3$ groups, is shown projected on the three axial planes. The calcium atoms have positions which correspond exactly with those of a hexagonal close-packed lattice which has been uniformly distorted so that it fits the axes of aragonite. The distance of the calcium atom from the side of the rectangle in fig. 7 (A) is thus $b/6=0\cdot66$ Å. The CO_3 group lies in a plane perpendicular to the 'c' axis, and is at a distance $c/3 = 0\cdot95$ Å from the nearest plane containing Ca atoms. The three oxygen atoms are symmetrically situated around the carbon atom, at a distance of $1\cdot30$ Å from it, this being the distance between carbon and oxygen centres in calcite. In the projection on the (001) plane, the carbon atom is at the centre of the hexagonal cell formed by the calcium atoms. The figure will show how the atoms are disposed and renders unnecessary a more detailed description of this arrangement. The crystal is built up by the repetition of this cell. Allowing to calcium a 'weight' of 40, carbon 12, oxygen 16, we can proceed to calculate the effect of the structure of the various planes on their reflecting power. These numbers are proportional to the number of electrons in each atom when uncharged, the total for the $CaCO_3$ group being 100 on this basis of calculation.

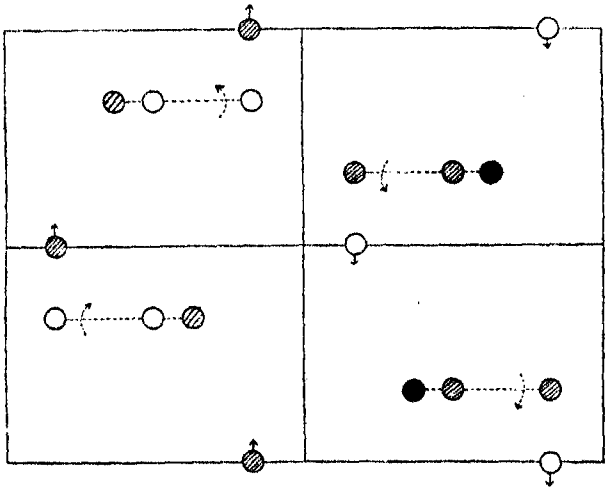
The factors for the different faces are as follows :—

Order.	1st.	2nd.	3rd.	4th.	5th.	6th.
(100)	36	100	36	100	—	—
(130)	36	100	36	100	—	—
(010)	0	32	36	32	0	100
(110)	0	32	36	32	0	100
(001)	10	10	100	10	10	100
(011)	2	30	0	14	24	36
(101)	42	10	36	10	—	—
(102)	24	44	0	10	—	—



A on plane '*a*, *b*.'

C on plane '*a*, *c*.'



B on plane '*b*, *c*.'

Fig. 7.—Projection of Unit Orthorhombic Cell on the three axial planes. The shading indicates the layers on which the atoms lie.

The observed spectra (fig. 2) have the following characteristics:—

(100 and (130) Large first and second order, nearly equal. Small third and fourth order, nearly equal.

(010) and (110) No first order. Third order large, no fifth order, sixth order large.

(001) First and second orders in normal ratio, but small. Third order large. Sixth order measurable, while fifth order is absent.

(011) No first order, large second order, no third order; fourth, fifth and sixth orders nearly equal.

(101) Large first order, second and third orders small and nearly equal.

(102) Large first and second orders, no third or fourth order.

The correspondence between the spectra and the calculated factors is very close, and extends to the high orders. This means that the atoms cannot be moved far from the symmetrical positions without destroying the correspondence. The simplified structure of fig. 7 must be close to the truth.

7. The factors will be altered by small symmetrical displacements of the atoms from the positions defined by fig. 7. A comparison of the (010) and (110) spectra shows that some displacement is necessary, for otherwise the intensities of corresponding orders should be almost identical for the two faces. These intensities are as follows:—

Order.	1st.	2nd.	3rd.	4th.	5th.	6th.
(010)	0	22·7	17·1	7·7	0	4·8
(110)	0	55·1	18·6	3·0	1·5	7·05

The second order from (110) is much stronger than that from (010). I have repeated this measurement on natural and ground faces of several crystals to confirm the difference. In expressing the structure of any set of planes, it is convenient to take some one plane symmetrically situated as a reference plane and state the phase difference between waves reflected by atoms in this plane and other sheets of atoms parallel to it. The (010) and (110) planes of fig. 7 are built up as follows:—

Central plane.	Carbon atom.	Mass 12.
± 60°	Two Oxygen atoms	,, 32
±120°	Oxygen atom	,, 16
±120°	Calcium atom	,, 40

The calcium atoms may be moved parallel to the '*b*' axis. If their phase is to be altered by 1°, it corresponds to a movement of 0·011 Å. Increasing the phase difference for the (010) planes involves a decrease of the phase difference for the (110) planes by half as much ; fig. 7 will make this clear, the arrows representing a movement of the Ca atoms which increases the phase difference for (010). The table shows the alteration in the factors produced (*a*) by moving the calcium atoms alone by an amount which alters the phase difference by 5° to 125°, (*b*) by moving the CO_3 group as a whole by 5° in the direction of the arrows, (*c*) by a combined movement of 6° for the calcium atoms and 4° for the CO_3 groups.

Factors for (010) *planes.*

Simple arrangement	0	32	36	32	0	100
(*a*)	2	26	35	42	12	95
(*b*)	2	23	37	49	6	87
(*c*)	2·5	18	34	55	14	87

The factors for the (110) planes will be altered in the opposite direction by a smaller amount. If the (010) and (110) spectra are compared, it will be seen that any of these distortions is of the right type to explain the difference between them. (020) is diminished and (220) increased, (030) and (330) remain unaltered, (040) is increased and (440) diminished, and (060) is diminished. A later comparison will show that the displacement (*c*) alters the factors by an amount of the right order. It is not possible to deduce the exact configuration from the observations. I believe, however, that the Ca atoms and CO_3 groups must be displaced slightly in the direction of the arrows in fig. 7, and that the algebraic sum of the displacements is about one-tenth of an Ångström unit (10° phase difference corresponds to 0·11 Å).

The (100) spectra have the following intensities :—

Order	1st	2nd	3rd	4th
	83	61·5	6·8	3·5

The factors for the first approximation in paragraph 6 are correct for planes of composition CaCO interleaved half-way by planes of composition O_2. This is not exactly true even for the symmetrical arrangement. If the carbon and oxygen centres are 1·30 Å apart, as in calcite, and the group is perfectly symmetrical, the oxygens will lie on either side with a phase difference of 163° and not of 180° for the first order. The factors for a few phase differences are given below.

180°	36	100	36	100	36
165°	37	96	45	84	60
160°	38	92	52	73	73
155°	39	88	60	62	86

A phase difference of 163° is in good accord with the observed spectra, where the fourth order is only about one half the third. Conversely, the (100) spectra and pseudohexagonal symmetry combine to show that the CO_3 group has very nearly the same shape in aragonite as in calcite.

The (130) spectra have the same relationship to each other as the (100) spectra, but appear to be weaker. The above arrangement of atoms does not explain this satisfactorily. Movements of the atoms parallel to the '*b*' axis affect the (130) spectra and not the (100) spectra, but I have not been able to find a set of displacements which weakens all the (130) spectra. Either the measurements are inaccurate, or the displacements suggested above must be further modified.

It may be claimed, however, that the general agreement for the whole series of planes around the '*c*' zone is good, when the symmetrical arrangement of paragraph 6 has been slightly modified by shifts of the Ca atoms and CO_3 groups of the type specified above (*c*), and when the carbon atom is surrounded symmetrically by three oxygen atoms at a distance of 1·30 Å.

In considering these planes, we are only concerned with the projection of the crystal structure on the '*ab*' plane, and need not take into account movements of the atoms parallel to the '*c*' axis. We have determined the values of the five parameters which modify the aspect of this projection.

The structure of planes which are not in the '*c*' zone involves the remaining four parameters, which fix displacements parallel to the '*c*' axis. The calcium atom may be moved up or down, and the CO_3 groups moved up or down and tilted, in any way which is consistent with symmetry about the reflexion plane parallel to the '*b*' and '*c*' axes. The symmetrical structure of fig. 7 again explains so closely the features of the spectra that I think it must be very close to the truth. The calcium atoms lie very nearly on the planes of the structure shown in fig. 7, and the atoms of the CO_3 group lie very nearly in a plane perpendicular to the '*c*' axis and at a distance $c/3$ from the plane containing the calcium atoms. In the case of the (001) spectra, a movement of the CO_3 group as a whole of 0·1 Å further away from the Ca planes would destroy the second order spectrum. A further movement which recreates this spectrum is out of the question. The (001) plane gives a measurable sixth order, although the corresponding glancing angle is so large. This shows that the fundamental spacing must be divided into three very exactly by the CO_3 groups. The CO_3 group may be tilted slightly so that the unique oxygen atom approaches by 0·1 or 0·2 Å the nearest Ca (001) plane. This tilt is shown by the arrows in the projection on the '*bc*' plane of fig. 7. It becomes, then, more nearly equidistant from the three surrounding calcium atoms, and its shift would explain the rather large (004) spectrum. The (011) spectra are peculiar, in that, of the odd orders (1st, 3rd, 5th and 7th), the only one which can be detected is the 5th. This is explained satisfactorily by the simple arrangement, whereas any large movement of the Ca atoms or CO_3 groups parallel to the '*c*' axis should give rise to an appreciable 3rd order spectrum.

There may be a small displacement of the Ca atoms parallel to the '*c*' axis. In the simple arrangement, these atoms do not contribute anything to the (102) 1st order spectrum, and this is found to be rather too large to be accounted for by the CO_3 groups alone. A movement of the Ca atoms in the direction of the arrows in fig. 7 adds to its strength, so it may well be that the Ca atoms have been displaced. A shift of 0·05 Å explains the large (102) spectrum. The (011) spectra, however, are considerably modified by such a shift, the fifth order then becoming much larger than the sixth order, which is contrary to experiment.

I do not believe the experimental observations are sufficiently accurate to determine the directions and amounts of these distortions, but I have entered into the above analysis to show how small they must be. In most cases shifts of the atoms of the order 1/20 Å alter the factors sufficiently to account for discrepancies between the simple structure of fig. 7 and the observations, and greater shifts destroy the correspondence. These shifts are almost too small to be shown in fig. 7, being of the order of 0·25–0·5 millimetre, so the structure must represent that of aragonite very closely.

8. A model of the aragonite structure, which has the form of fig. 7, but in which the calcium atoms and CO_3 groups have been displaced in the direction of the '*b*' axis by the '6°, 4°' shift described in the preceding paragraph, will be assumed as a close approximation to the real structure. The amplitude factors for *all* the planes and orders can now be calculated, and compared with the observed intensities. This is a more searching test of the correctness of the model than a comparison of orders for any one face.

The principal difficulty in carrying out such a test is due no doubt as to the relative scattering power of the atoms at various angles. The amplitude of the wave diffracted by each atom falls off very rapidly as the angle, through which it is diffracted, increases, and it falls off in a different way for each atom. It is almost certainly the case that the relative scattering power of calcium and oxygen atoms vary greatly at different angles. The values 40 for calcium, 16 for oxygen, 12 for carbon have been assumed in the lack of a more complete knowledge as a first approximation.

The following table shows the results of the correlation :—

Face.	Sin θ.	Observed intensity	Amplitude factor/100.	$\frac{\text{Intensity}}{\text{factor.}}$
011	0·0662	abs.	0·5	—
110	0·0732	abs.	0·2	—
010	0·0774	abs.	2·5	—
001	0·1074	30·0	10·0	3·00
102	0·1241	88·0	31·7	2·75
100	0·1241	83·0	38·0	2·19
130	0·1317	53·0	35·5	1·49
022	0·1324	54·0	33·0	1·64
220	0·1464	55·0	35·0	1·57
020	0·1548	22·7	18·4	1·23
101	0·1643	60·0	50·5	1·19
033	0·1986	abs.	0·0	—
002	0·2148	6·2	10·0	0·62
330	0·2196	18·6	36·7	0·505
030	0·2322	17·1	34·1	0·500
204	0·2482	21·5	41·0	0·523
200	0·2482	61·5	92·5	0·666
260	0·2634	37·0	97·1	0·381
044	0·2648	3·25	9·2	0·353
440	0·2928	3·5	24·2	0·144
040	0·3096	7·7	55·2	0·139
003	0·3222	16·0	100·0	0·160
202	0·3286	2·0	32·0	0·062
055	0·3310	4·9	27·0	0·181
550	0·3600	1·5 ?	2·0	—
306	0·3723	abs.	0·0	—
300	0·3723	6.8	52·0	0·131
059	0·3870	abs.	14·0	—
390	0·3951	4·0	33·0	0·121
066	0·3973	4·5	34·2	0·128
004	0·4296	2·3	10·0	0·230
660	0·4392	7·05	94·3	0·075
060	0·4644	4·8	86·7	0·055
303	0·4929	2·7	52·0	—
400	0·4964	3·5	73·5	0·047
4.12.0	0·5268	2·0	88·4	0·023
005	0·5370	abs.	10·0	—
006	0·6444	1·0	100·0	0·010

The intensity is modified by continuous factors which vary regularly with the glancing angle, and by the amplitude-factor peculiar to each plane and order. The former need not be taken into account for the present purpose, as they cause a regular falling off of intensity towards the higher orders. If the figures in the third and fourth columns are compared, it will be seen that in nearly every case large intensities are associated with large amplitude-factors and *vice versa*. Even though the relative scattering power of the atoms must depart considerably from the 40, 12, 16 ratio, this correspondence is a check on the correctness of the model.

We would expect the observed intensity to vary as the square of the amplitude-factor, since the amplitude of the wave reflected at a single plane is proportional to the latter. The figures in the last column show that the intensity appears to be *proportional to the amplitude-factor and not to its square*. This confirms a very interesting series of experiments made on calcite by W. H. Bragg,* in which he got exactly the same result. The structure of calcite involves only one parameter, and consequently may be regarded as accurately known.

The following figures are taken from W. H. Bragg's paper; I have made an approximate comparison of the (100) and (222) calcite spectra with NaCl (200) in order to express the intensities given by aragonite and calcite on the same scale:—

Spectra yielded by Calcite.

Face.	Sin θ.	Observed intensity.	Amplitude-factor/100.	$\frac{\text{Intensity}}{\text{factor.}}$
111	0·0810	34·0	12	2·83
100	0·1010	149·0	68	2·19
111	0·1080	37·0	20	1·85
110	0·1240	47·0	36	1·31
110	0·1610	61·0	68	0·89
222	0·1620	34·0	36	0·94
200	0·2020	18·0	36	0·50
211	0·2140	38·0	68	0·56
222	0·2160	58·0	100	0·58
111	0·2430	3·7	12	0·31
220	0·2480	12·5	36	0·35
300	0·3030	15·0	68	0·22
220	0·3220	6·4	36	0·18
444	0·3240	21·0	100	0·21
333	0·3240	abs.	20	—
330	0·3720	3·6	36	0·10
400	0·4040	6·7	100	0·067
444	0·4320	7·0	100	0·070
330	0·4830	2·8	68	0·041
440	0·4960	2·6	100	0·026

The comparison between the figures for calcite and aragonite is very interesting since the composition of the crystals is the same. The quotient intensity/factor is smaller for calcite than for aragonite at corresponding angles, but there is a close parallelism between the two sets of figures.

Some of the discrepancies in the tables between observed intensities and amplitude-factors may be due to errors in calculating the latter. It does not seem profitable to discuss the theoretical significance of the apparent proportionality between factor and intensity until the factors can be calculated with more certainty. Apparently some effect such as "extinction factor" is diminishing the strong reflexions far more than the weak ones. The experiments of W. H. Bragg have shown that the proportionality exists in calcite, where we are dealing with a very simple structure and are in no doubt as to the composition of the various planes. The fact that the model for aragonite, which is proposed here, leads to a similar empirical result, is additional evidence of its correctness.

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* W. H. Bragg, 'Phil. Trans. Roy. Soc.,' A, vol. 215 (1915).

9. In the aragonite structure the calcium atoms lie very close to positions which would give the crystal hexagonal symmetry. The arrangement of the CO_3 groups, however, causes the symmetry to be definitely orthorhombic. All CO_3 groups which lie in a row parallel to the '*a*' axis are similarly oriented, whereas groups which lie nearly in a row parallel to the face (110) point alternate ways, and are displaced up and down in the direction of the '*c*' axis. Such a row is shown in fig. 8, where it is enclosed between two dotted lines. The crystal twins about the plane (110), and a possible reason for this is suggested in the figure. The section of the crystal between the dotted lines would serve as origin for the growth of either system shown on each side of it, the direction of the row of similarly oriented CO_3 groups (the '*a*' axis) being turned through nearly 60° in crossing the plane of twinning.

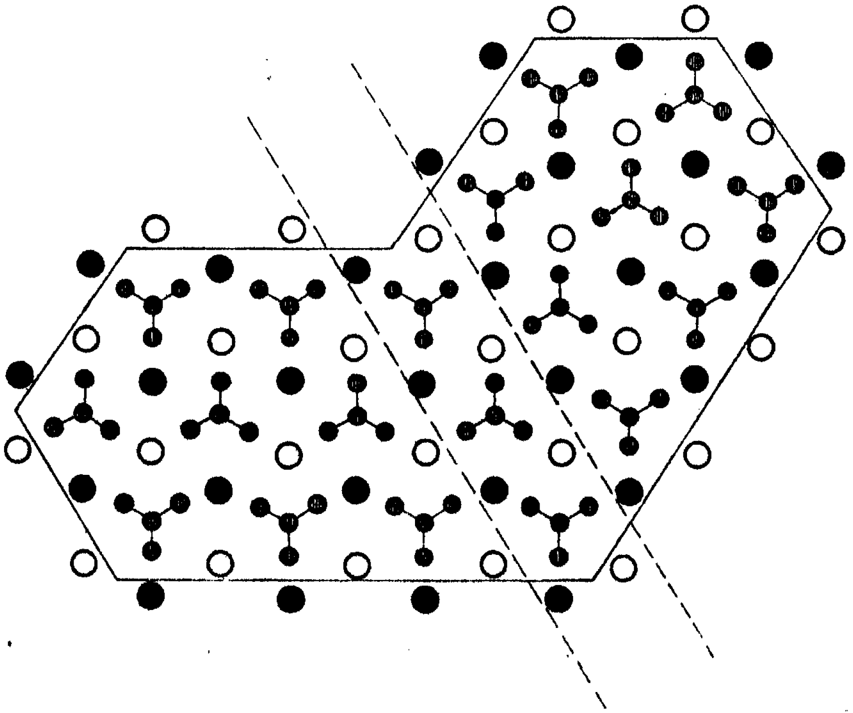

FIG. 8.—Section perpendicular to '*c*' axis of Aragonite twinned on (110).

A correspondence has been traced above between the dimensions of the aragonite and calcite structures. In both the calcium atoms lie on layers which succeed each other at a distance of 2·86 Å. In calcite the atoms in a layer lie at the corners of equilateral triangles whose sides are 4·96 Å. In aragonite one side of the corresponding triangle is 4·94 Å, and the other two are approximately equal to 4·66 Å. They may be greater if the layer is puckered by movements of the Ca atoms parallel to the 'c' axis. In calcite the distance between centres of calcium and oxygen atoms is 2·38 Å. In aragonite, since the oxygen atoms are in the larger space between three calcium atoms, this distance is increased. For the simple model which has been assumed above, the distances are as follows :—

Unique oxygen atoms to three surrounding calcium atoms,
2·28 Å, 2·64 A, 2·64 A.

Other oxygen atoms to three surrounding calcium atoms,
2·47 Å, 2·60 Å, 2·45 Å.

In the case of the first oxygen atom, the large difference between the three distances suggests that the model must be corrected, the atom being moved so as to equalise the distances. Such a movement is shown by the arrows in fig. 7, and its existence is not precluded by the observed spectra. The mean distance between atomic centres is 2·51 Å, as against 2·38 Å. in calcite. The calcium atom is surrounded by nine oxygen atoms, six of the one sort and three of the other. It would appear that the CO_3 group has approximately the same dimensions in both crystals, the distance between oxygen and carbon centres being 1·30 Å. In all cases errors of 0·05 Å in fixing the position of the atom must be regarded as possible, and in some cases the error may be greater. This is due mainly to uncertainty in calculating the amplitude-factor and not to error in measuring intensities of reflexion.

Summary.

The aragonite structure is based on the simple orthorhombic lattice (Γ_0). The cell, whose sides are 4·94 Å, 7·94 Å, 5·72 Å, contains four molecules of $CaCO_3$. The elements of symmetry form the space group Q_h^{16}.

The structure is built of Ca atoms and CO_3 groups, which have a form almost identical with the CO_3 groups in calcite.

The calcium atoms are arranged on a distorted hexagonal close-packed point system, intimately related in its dimensions to the distorted cubic close-packed point system of the calcium atoms in calcite.

The CO_3 groups in aragonite are arranged differently to the corresponding groups in calcite, each oxygen atom being surrounded by three calcium atoms in the former crystal, and two in the latter. Considered as a whole, the CO_3 group lies between two groups of three Ca atoms in both crystals.

A comparison of the observed intensities and calculated amplitude-factors for aragonite supports an empirical law discovered by W. H. Bragg in examining calcite. The intensity appears to be proportional to the amplitude-factor, and not to its square as theory would suggest.

The twinning of the aragonite crystal about the plane (110) is simply explained by the structure which is ascribed to it.

I wish to express my thanks to Dr. Hutchinson, F.R.S., of Pembroke College, Cambridge, and to Dr. Gordon, of King's College, London, for supplying me with crystals of aragonite. I am indebted to Mr. Vernon, Lecturer in Physics at Manchester University, for a number of careful and accurate measurements of intensity of reflexion. The investigations were carried out with Coolidge tubes generously presented to my department by the Research Laboratory of the General Electric Company, Schenectady. Other apparatus has been purchased with the aid of a grant made by the Government Grant Committee of the Royal Society.

[*Note added* 17.12.23.—In fig. 7 (B) an error has been made in the arrangement of the groups. The figure is a correct representation of the projection of the unit cell on the '*b*, *c*' plane, but, in order that it may correspond to figures 7 (A) and 7 (C), the two rectangles on the right-hand side should be transferred, without change in orientation, to the left-hand side of the figure, and the two on the left transferred to the right-hand side.]

Constitution of the X-Ray Spectra belonging to the L Series of the Elements.

By H. Hirata.

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§ 1°. *Lines belonging to the L-series and their wave-lengths.*

The X-ray spectra, as are well known, consist of three groups of lines, *i.e.*, K, L, M, series.

The lines mentioned in order of increasing wave-lengths (roughly, because some lines interchange their position for different elements), are

for K-series :—

$K_{\alpha 2}$, $K_{\alpha 1}$, $K_{\beta 3}$, $K_{\beta 1}$, $K_{\beta 2}$.

for L-series :

Ll, $L_{\alpha 2}$, $L_{\alpha 1}$, $L_{\alpha 3}$, L_{γ}, $L_{\beta 4}$, $L_{\beta 6}$, $L_{\beta 1}$, $L_{\beta 3}$, $L_{\beta 2}$, $L_{\beta 8}$, $L_{\beta 7}$, $L_{\beta 5}$,
$L_{\beta 9}$, $L_{\beta 5}$ (o.s.), $L_{\gamma 5}$, $L_{\gamma 1}$, $L_{\gamma 7}$, $L_{\gamma 6}$, $L_{\gamma 2}$. $L_{\gamma 3}$, $L_{\gamma 4}$,

for M-series :

$M_{\alpha 2}$, $M_{\alpha 1}$, M_{β}, M_{ρ}, M_{δ}, M_{ϵ}.

With regard to the wave-lengths of L series many experimental data have been obtained by numerous authors, among which let us select the values given in D. Coster's paper* and rely on them in our further arguments, as it seems to me quite complete for all the elements between tantalum and uranium.

From these numerical values of the wave-lengths, we can get the value of ν/N as shown in Table I, where ν is the wave number and in cm.$^{-1}$ and N Ryberg's constant, which is equal to 109737 cm.$^{-1}$.

In this table, the values in $(\quad)_o$, $(\quad)_s$ are interpolated from the measurements of Overn† and Siegbahn‡ and those in $[\quad]_s$ are interpolated or extrapolated from the old data of Siegbahn and Friman.§

To get rid of the effect of the general shift of all the experimental values of the wave-lengths of the lines, due to the difference of the numerical values given to the grating constants of the crystals used, all the interpolations are so made that the ratio of the distances between an interpolated line and its neighbouring lines on both sides is equal to the corresponding ratio in the data used, *i.e.*, equal to the ratio of the distances between the original line to be interpolated and its neighbouring lines on both sides.

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* D. Coster, 'Z. f. Phys.,' vol. 6, p. 188 (1921).

† O. B. Overn, 'Phys. Rev.,' vol. 14, p. 137 (1919).

‡ M. Siegbahn, 'Phil. Mag.,' vol. 38, p. 639 (1919).

§ M. Siegbahn and E. Friman, 'Phys. Zeits.,' vol. 17, pp. 17, 61, 176 (1916); 'Ann. d. Phys.,' vol. 49, p. 623 (1916).

The notations in ( ) on the right side of the names of lines are their other names given by Sommerfeld,[*] and the signs (α) and (β) under the names of lines express the groups specified by Overn,[†] to which the line belongs. Among those lines there is a line β_5(o.s.) which is the line denominated β_5 by Overn and Siegbahn.

§ 2°. *The Effective Nuclear Charge of an Atom.*

Sommerfeld[‡] has deduced a formula for the frequencies of the so-called "Wasserstoffähnlich" spectra from Bohr's theory and his own theory of elliptic orbits by making an excellent application of the quantum theory. Then, considering the K and L terms of the X-ray spectra as being "Wasserstoffähnlich" he extended his deduction to the X-ray spectra by putting the so-called "Effective nuclear charge" in the place of the actual nuclear charge.

According to his theory, two possible orbits—circular and elliptic—should correspond to L terms, and consequently the lines of K and L series, which contain an L term in their frequency formula, should be doublets. The frequency difference $\Delta\nu$ of their components is,

$$\Delta\nu = L_2 - L_1 \doteqdot \frac{N\alpha^2}{2^4}(Z - l)^4 \quad \dots\dots\dots\dots\dots\dots (1)$$

where

$$\alpha = \frac{2\pi e^2}{hC} = 7 \cdot 29 \times 10^{-3},$$

h : Planck's constant $= 6 \cdot 55 \times 10^{-27}$ erg sec.
c : velocity of light $= 3 \times 10^{10}$ cm. sec.$^{-1}$.
e : electronic charge $= 4 \cdot 77 \times 10^{-10}$ E.S.U.
N : Ryberg's frequency $= 109737$ cm.$^{-1}$.
$(Z - l)\,e$: effective nuclear charge.
Z : atomic number of the element under consideration.
l : a certain constant.

In the above expression (1) L_1 and L_2 are the L terms corresponding to the circular and elliptic orbits respectively, whose azimuth and radial quantum

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[*] A. Sommerfeld, 'Ann. der Physik,' vol. 51, p. 133 (1916); 'Atombau u. Spectrallinien,' Zweite Auf., 3 Kap., p. 164.

[†] O. B. Overn, 'Phys. Rev.,' vol. 14, p. 137 (1919).

[‡] A. Sommerfeld, 'Ann. der Physik,' vol. 51, p. 44 (1916).

Table I.—The Values of

Atomic Number.	l (ϵ)	α_2 (α')	α_1 (α)	α_3 (α'')	γ (γ)	β_4 (υ)	β_6	β_1 (β)	β_3 (ϕ)	β_2 (μ)
30 Zn ..	—	—	[73·8]$_s$	—	—	—	—	—	—	—
33 As ..	—	—	[93·0]$_s$	—	—	—	—	[96·44]$_s$	—	—
35 Br ..	—	—	[108·6]$_s$	[109·0]$_s$	—	—	—	[111·9]$_s$	—	—
37 Rb ..	—	—	[124·2]$_s$	[124·7]$_s$	—	—	—	[128·5]$_s$	—	—
38 Sr ..	—	—	[132·5]$_s$	—	—	—	—	[137·3]$_s$	—	—
39 Y ..	—	—	[141·0]$_s$	[141·5]$_s$	—	—	—	[146·3]$_s$	—	—
40 Zr ..	—	—	[149·8]$_s$	[150·4]$_s$	—	—	—	[155·7]$_s$	—	—
41 Nb ..	—	[159·0]$_s$	[159·2]$_s$	[159·6]$_s$	—	—	—	[165·9]$_s$	—	[171·4]$_s$
42 Mo ..	—	[168·4]$_s$	[168·7]$_s$	[169·3]$_s$	—	—	—	[176·1]$_s$	—	—
44 Ru ..	—	[187·8]$_s$	[188·1]$_s$	[188·9]$_s$	—	—	—	[196·8]$_s$	—	—
45 Rh ..	—	—	[198·3]$_s$	[199·1]$_s$	—	—	—	[208·4]$_s$	—	—
46 Pd ..	—	[208·3]$_s$	[208·8]$_s$	[209·4]$_s$	—	[223·8]$_s$	—	[219·9]$_s$	[226·1]$_s$	[233·4]$_s$
47 Ag ..	—	[219·3]$_s$	[219·8]$_s$	[220·5]$_s$	—	[236·0]$_s$	—	[232·0]$_s$	[238·4]$_s$	[246·4]$_s$
48 Cd ..	—	[230·2]$_s$	[230·8]$_s$	—	—	[247·9]$_s$	—	[244·1]$_s$	[250·4]$_s$	[259·3]$_s$
49 In ..	—	[241·5]$_s$	[242·0]$_s$	—	—	—	—	[256·7]$_s$	—	[271·7]$_s$
50 Sn ..	—	[252·8]$_s$	[253·6]$_s$	—	—	[273·1]$_s$	—	[269·5]$_s$	[276·1]$_s$	[287·3]$_s$
51 Sb ..	—	[264·7]$_s$	[265·4]$_s$	—	—	[286·2]$_s$	—	[282·8]$_s$	[289·4]$_s$	[301·6]$_s$
52 Te ..	—	[276·2]$_s$	[277·0]$_s$	—	—	[299·4]$_s$	—	[296·4]$_s$	[303·0]$_s$	[316·3]$_s$
53 J ..	—	[288·8]$_s$	[289·7]$_s$	—	—	[313·0]$_s$	—	[310·6]$_s$	[317·2]$_s$	[331·4]$_s$
55 Cs ..	—	[314·3]$_s$	[315·2]$_s$	—	—	[341·6]$_s$	—	[339·5]$_s$	[346·6]$_s$	[362·5]$_s$
56 Ba ..	—	[327·1]$_s$	[328·3]$_s$	—	—	[356·2]$_s$	—	[354·7]$_s$	[361·6]$_s$	[378·6]$_s$
57 La ..	—	[340·8]$_s$	[341·9]$_s$	—	—	[371·5]$_s$	—	[370·3]$_s$	[377·5]$_s$	[395·0]$_s$
58 Ce ..	—	[354·2]$_s$	[355·5]$_s$	—	—	[386·6]$_s$	—	[386·3]$_s$	[395·0]$_s$	[412·0]$_s$
59 Pr ..	—	[368·6]$_s$	[370·1]$_s$	—	—	—	—	[403·4]$_s$	[411·0]$_s$	[429·8]$_s$
60 Nd ..	—	[383·0]$_s$	[384·7]$_s$	—	—	[420·5]$_s$	—	[420·5]$_s$	[428·2]$_s$	[447·6]$_s$
62 Sm ..	—	[412·3]$_s$	[414·2]$_s$	—	—	—	—	[455·6]$_s$	[463·8]$_s$	[483·7]$_s$
63 Eu ..	—	[427·6]$_s$	[429·6]$_s$	—	—	[473·9]$_s$	—	[475·1]$_s$	[482·7]$_s$	[503·5]$_s$
64 Gd ..	—	[443·7]$_s$	[446·0]$_s$	—	—	[492·3]$_s$	—	[494·2]$_s$	[503·2]$_s$	[522·5]$_s$
65 Tb ..	—	[459·5]$_s$	[461·0]$_s$	—	[470·9]$_s$	[510·8]$_s$	—	[513·4]$_s$	[522·2]$_s$	[541·8]$_s$
66 Ps ..	—	[475·6]$_s$	[477·9]$_s$	—	—	[529·5]$_s$	—	[533·2]$_s$	[541·5]$_s$	[561·8]$_s$
67 Ho ..	—	[491·5]$_s$	[494·4]$_s$	—	—	[550·0]$_s$	—	[553·6]$_s$	[562·5]$_s$	[581·2]$_s$
68 Er ..	—	[508·0]$_s$	[511·1]$_s$	—	[528·3]$_s$	[569·9]$_s$	—	[574·6]$_s$	[584·1]$_s$	[601·9]$_s$
70 Ad ..	[481·6]$_s$	[542·1]$_s$	[545·7]$_s$	—	[563·2]$_s$	[611·6]$_s$	—	[618·2]$_s$	[628·0]$_s$	[644·5]$_s$
71 Cp ..	[496·9]$_s$	[559·4]$_s$	[562·9]$_s$	—	—	[634·1]$_s$	—	[641·3]$_s$	[651·4]$_s$	[666·1]$_s$
73 Ta ..	528·50	595·83	600·20	—	621·83	678·93	686·87	688·51	699·23	711·42
74 W ..	544·02	613·85	618·45	—	642·78	701·66	708·03	712·39	723·23	733·76
76 Os ..	—	651·75	656·45	—	—	748·25	756·33	762·83	774·08	780·58
77 Ir ..	—	670·35	675·84	—	—	774·62	777·75	788·09	800·82	804·39
78 Pt ..	608·64	689·73	695·58	—	734·82	799·52*	799·52*	815·65	828·80*	823·80*
79 Au ..	625·63	709·22	715·53	—	759·97	825·15	820·51	843·02	—	853·46
80 Hg ..	—	[727·3]$_s$	[738·4]$_s$	—	—	—	—	[868·7]$_s$	—	[872·66]$_s$
81 Tl ..	—	749·37	756·42	—	810·30	878·64	869·49	899·88	919·23	904·1
82 Pb ..	676·70	769·96	777·51	—	835·90	907·01	894·50	929·98*	933·30	929·98*
83 Bi ..	694·07	790·20	798·54	—	862·32	934·22	918·97	959·93	973·85	956·28
84 Po ..	—	—	[832·2]$_s$	—	—	—	—	[990·5]$_s$	—	—
88 Ra ..	—	—	[905·8]$_s$	—	—	—	—	—	—	—
90 Th ..	819·19	944·08	955·78	—	—	1155·00	1102·78	1194·94*	1211·67	1151·93
92 U ..	855·84	990·37	1003·23	—	1184·95	1222·53	1158·70	1269·08	1286·29	1210·70

numbers are, according to Sommerfeld's notation, $n = 2$, $n' = 0$, and $n = 1$, $n' = 1$ respectively. With regard to l, Sommerfeld gives $l = 3\cdot63$, because this value agrees with observations.

As it is represented in several papers (*e.g.*, see Table 3 in D. Coster's paper),* the differences of frequencies between the L doublets, *i.e.*, $L\gamma$—L_1, $L\beta_2$—$L\alpha_2$, $L\gamma_5$—$L\beta_6$, $L\gamma_2$—$L\beta_3$, and $L\gamma_6$—$L\beta_5$, are not only nearly equal to each other but also agree nearly with the theoretical value calculated from (1) putting $l = 3\cdot63$, and with the difference of L-absorption edges examined by Duane and Patterson† and many other authors‡, which is considered to be equal to the difference of the frequencies corresponding to L_1 and L_3 terms.

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* D. Coster, 'Z. f. Physk.,' vol. 6, p. 191 (1921).

† W. Duane and R. A. Patterson, 'Proc. Nat. Acad. Sci.,' Washington, Sept., 1920.

‡ G. Herts, 'Z. f. Physk.,' vol. 3, p. 19 (1920); M. de Broglie, 'C.R.,' vol. 158, p. 1493 (1914).

$\frac{\nu}{N}$ in the L Series.

β_6	β_7	β_8	β_9	β_5 (ο-δ) (ρ)	γ_5	γ_1 (δ)	γ_7	γ_6	γ_2 (θ)	γ_3 (χ)	γ_4 (ψ)
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	[169·2]$_S$	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	[245·0]$_S$	—	—	[253·3*]$_S$	[253·3*]$_S$	—
—	—	—	—	—	—	[259·3]$_S$	—	—	—	—	—
—	—	—	—	—	—	[273·6]$_S$	—	—	—	—	—
—	—	—	—	—	—	[288·4]$_S$	—	—	—	—	—
—	—	—	—	—	—	[303·9]$_S$	—	—	[313·9]$_S$	[315·4]$_S$	[321·9]$_S$
—	—	—	—	—	—	[319·9]$_S$	—	—	[327·6*]$_S$	[327·6*]$_S$	—
—	—	—	—	—	—	[336·0]$_S$	—	—	—	—	—
—	—	—	—	—	—	[352·8]$_S$	—	—	—	—	—
—	—	—	—	—	—	[387·8]$_S$	—	—	[407·9*]$_S$	[407·9*]$_S$	—
—	—	—	—	—	—	[405·9]$_S$	—	—	—	—	—
—	—	—	—	—	—	[424·6]$_S$	—	—	—	—	—
—	—	—	—	—	—	[444·1]$_S$	—	—	[455·0*]$_S$	[455·0*]$_S$	—
—	—	—	—	—	—	[465·4]$_S$	—	—	[470·5]$_S$	[471·4]$_S$	—
—	—	—	—	—	—	[486·0]$_S$	—	—	[505·4]$_S$	[513·4]$_S$	—
—	—	—	—	—	—	[528·8]$_S$	—	—	[549·3*]$_S$	[549·3*]$_S$	—
—	—	—	—	—	—	[548·3]$_S$	—	—	[569·9]$_S$	[573·1]$_S$	—
—	—	—	—	—	—	[570·6]$_S$	—	—	[583·4]$_S$	[584·9]$_S$	—
—	—	—	—	[580·3]$_S$	—	[595·2]$_S$	—	—	[617·0]$_S$	[619·9]$_S$	[634·1]$_S$
—	—	—	—	—	—	[619·9]$_S$	—	—	[640·8]$_S$	[642·6]$_S$	—
—	—	—	—	—	—	[644·0]$_S$	—	—	[665·6]$_S$	[667·6]$_S$	—
—	—	—	—	—	—	[666·6]$_S$	—	—	[688·8]$_S$	[692·5]$_S$	—
—	—	—	—	[640·8]$_S$	—	[719·2]$_S$	—	—	[742·1]$_S$	[745·1]$_S$	—
—	—	—	—	—	—	[744·5]$_S$	—	—	[767·1]$_S$	[770·3]$_S$	—
715·60	723·30	728·65	—	—	778·86	803·04	—	820·98	826·90	831·28	857·74
737·60	746·45	751·56	(753·74)$_G$	(756·87)$_S$	807·03	831·81	(845·180)$_G$	854·08	854·08	859·97	887·77
—	—	789·65	—	—	—	891·25	—	—	—	—	—
808·82	—	826·18	—	[827·7]$_S$	—	921·96	—	945·64*	945·67*	952·64	—
833·90	844·93	851·57	—	[850·1]$_S$	924·71	953·77	—	978·07*	978·07*	984·52	1018·17
858·94	870·77	877·70	—	[880·5]$_S$	955·01	985·88	—	1011·12*	1011·12*	1017·41	1051·86
—	—	—	—	—	—	[1011·4]$_S$	—	—	—	—	—
—	922·64	931·47	—	[932·7]$_S$	1019·14	1053·12	—	1082·69	1078·83	1087·54	1125·00
936·03	950·22	959·72	—	—	1054·83	1088·37	—	1110·97*	1113·87*	1119·97*	1162·89
—	—	987·98	—	[987·3]$_S$	1087·75	1124·10		1157·55*	1140·20	1157·55*	1196·80
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	1194·94*	—	—	—	1390·74	—	1446·20	—	—	—
1265·91	1238·14	1258·43	—	—	—	1486·98	—	1537·76	1507·82	1526·41	—

From the experimental data of the wave numbers of the Lα_2 and Lβ_2 lines in Table I, and from those of the Kα_2 and Kα_1 lines given by Siegbahn and Stenstrom* the wave number differences of K and L doublets are obtained as shown in Table II.

The elements arranged in the same section in Table II are the elements belonging to the same row in Periodic system.

The values of $\Delta\nu/(Z-l)^4$, calculated from the values of $\Delta\nu/N$ in this table should be constant—according to Sommerfeld's theory—for all elements and for any doublet in the L and K series, and equal to the frequency differences between the components of hydrogen doublets $\Delta\nu_H$ whose numerical value is

$$\Delta\nu_H = 0\cdot365 \text{ cm.}^{-1}. \qquad (2)$$

Now, these are confirmed throughout nearly the whole domain of the systems of the elements as shown in Table II, but the agreement is never strict. In this table we can notice that (1) the values of $\Delta\nu/(Z-l)^4$ are always greater than the wave number difference between the components of hydrogen doublet $\Delta\nu_H = 0{\cdot}365$ (2) the values of $\Delta\nu/(Z-l)^4$ are always greater in the K series than in the L series for the same element. Especially is some elements as in (Z = 49), Pr (Z = 59), etc., this difference becomes so large as it corresponds to the displacement of the order 0·01 Å.U. in the lines belonging to the K series, or of the order of 0·04 Å.U. in the lines of the L series.

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* M. Siegbahn u. W. Stenstrom, 'Physikal. Z.,' vol. 17, p. 48 and p. 318 (1916).

Table II.

Atomic No.		L Doublets.			K Doublets.		
		$\Delta\nu/N$.	$\Delta\nu$.	$\Delta\nu/(Z-l)^4$.	$\Delta\nu/N$.	$\Delta\nu$.	$\Delta\nu/(Z-l)^4$.
38	Sr				6·0	6·58·10^4	0·472
41	Nb	6·9	7·57 10^5	0·388	7·0	7·68 ,,	0·394
44	Ru	9·0	9·88 ,,	0·372	—	—	—
45	Rh	—	—	—	10·0	1·097·10^4	0·374
47	Ag	12·7	1·40 10^6	0·396	14·0	1·537 ,,	0·434
48	Cd	13·9	1·53 ,,	0·395	16·0	1·755 ,,	0·453
49	In	15·2	1·67 ,,	0·394	18·0	1·976 ,,	0·466
50	Sn	16·7	1·83 ,,	0·392	11·0	1·207 ,,	0·261
52	J	21·6	2·38 ,,	0·401	—	—	—
56	Ba	27·6	3·01 ,,	0·400	29·0	3·183 ,,	0·423
57	La	29·5	3·25 ,,	0·401	26·0	2·851 ,,	0·351
58	Ce	32·1	3·53 ,,	0·404	36·0	3·949 ,,	0·452
59	Pr	34·8	3·83 ,,	0·408	39·0	4·381 ,,	0·467
65	Tb	53·9	5·93 ,,	0·418	—	—	—
66	Dy	57·6	6·34 ,,	0·419	—	—	—
71	Lu	81·9	9·01 ,,	0·437	—	—	—
73	Ta	92·7	1·02 10^7	0·440	—	—	—
74	W	98·5	1·084 ,,	0·442	—	—	—
78	Pt	125·9	1·385 ,,	0·453	—	—	—
79	Au	133·8	1·472 ,,	0·456	—	—	—
83	Bi	168·3	1·851 ,,	0·468	—	—	—
90	Th	250·86	2·752 ,,	0·495	—	—	—
92	U	278·41	3·066 ,,	0·503	—	—	—

There are, however, a few exceptions to this law as in the cases of Sn and La ; but in such elements, Sommerfeld's theory itself does not always hold, because the frequency differences of their doublets become smaller than those of the elements of smaller atomic numbers. I cannot enter into the details of such a special case, (3) the doublets show a systematic rising of $\Delta\nu/(Z-l)^4$, and it looks rather likely that $\Delta\nu/(Z-l)^4$ remains nearly constant for the elements belonging to the same row of Periodic system.

It is due, according to Sommerfeld's explanation, to the fact that the value of $\Delta\nu/(Z-l)^4$ is obtained by neglecting the higher terms of the relativity correction. If we take into account the higher terms of the relativity correction, $\Delta\nu/(Z-l)^4$ should be expressed by the following formulæ :—

$$\frac{\Delta\nu}{(Z-l)^4}=\frac{(1.1)-(2.0)}{(Z-l)^4}$$

$$=\Delta\gamma_H\left\{1+\frac{5}{2}\,\frac{\alpha^2}{2^2}\,(Z=l)^2+\frac{53}{8}\,\frac{\alpha^4}{2^4}\,(Z-l)^4+\ldots\right\}\ldots.(3)$$

where

$$(n,\,n')=N\left(\frac{E}{e}\right)^2\left\{\frac{1}{(n+n')^2}+\frac{\alpha^2}{(n+n')^4}\left(\frac{E}{e}\right)^2\left(\frac{1}{4}+\frac{n'}{n}\right)+\ldots\right\}\ ..(3a)$$

Table III.—Relativity Correction.

Atomic Nos.		$\frac{5\alpha^2}{2}\frac{(Z-3\cdot63)^2}{2^3}$.	$\frac{53\,\alpha^4}{8}\frac{(Z-3\cdot63)^4}{2^4}$.	Numerical sum of the higher terms.	$\Delta\nu_H$.
41	Nb	0.04	0.00	0·04	0·373
44	Ru	0.05	0.00	0·05	0·354
47	Ag	0.06	0.00	0·06	0·374
48	Cd	0.06	0.00	0·06	0·372
49	In	0.06	0.00	0·06	0·371
50	Sn	0.07	0.00	0·07	0·366
53	J	0.08	0.00	0·08	0·371
56	Ba	0.08	0.01	0·09	0·367
57	La	0.09	0.01	0·10	0·365
58	Ce	0.10	0.01	0·11	0·364
59	Pr	0.10	0.01	0·11	0·368
65	Tb	0.12	0.02	0·14	0·367
66	Dy	0.12	0.02	0·14	0·368
71	Lu	0.14	0.02	0·16	0·377
73	Ta	0.15	0.02	0·17	0·376
74	W	0.15	0.03	0·18	0·375
78	Pt	0.17	0.04	0·21	0·374
79	Ag	0.18	0.04	0·22	0·374
83	Bi	0.19	0.05	0·24	0·377
90	Th	0.23	0.07	0·30	0·381
92	U	0.25	0.07	0·32	0·381

Table III shows the values of $\Delta\nu_H$ calculated from (2) giving to $\Delta\nu/(Z-l)^4$ the values in Table 2 successively. In this table we can see that the calculated values of $\Delta\nu_H$ still remain greater than 0·365 except Ru (44).

For the elements of higher atomic numbers as Th (90) U (92) it remains larger than 0·365 by the order of 0·02 cm.$^{-1}$ which corresponds to a discrepancy of over 0·015 Å.U. in wave-length differences between the lines $L\alpha'_2$ and $L\beta_1$ of the L doublets.

Considering these results it seems to me that Sommerfeld's theory holds only approximately, and in details further correction is needed.

Vegard* ingeniously obtained a formula showing the relation between the frequency and number of electrons in the orbits which are responsible for X-ray radiation. Adopting Bohr's assumption of the stable orbits of electrons in an atom, and by comparing his mathematical formula with the experimental data, he calculated the number of electrons in every orbit, and the radii of these orbits.

According to his result the number of the electrons in the orbits, which are responsible for X-ray radiation, are too immense to neglect their effects on the motion of an electron in the same or in the inner orbit; and that the radius of the innermost or K orbit is too large to consider as negligible compared with the magnitude of the outer orbits.

It seems to be quite legitimate to take into account the corrections due to these effects to the effective nuclear charge, and to consider the terms k—the correction for the K term corresponding to l for the L term—and l as the correction due to the effects of the remaining electrons in the atom. Consequently, the terms l and k should be variables according to the number and distribution of the electrons in the atom. The repulsion due to the outer electrons affects an inner electron as if the charge on the nucleus were large, and to the larger effective nuclear charge the smaller values of k, l terms must correspond. Therefore, the terms l, k are smaller in the case when radiation takes place in the region having more electrons outside.

Then we get the following conclusions from the above assumption:—

(1) The terms like k and l need not necessarily be positive integers and equal to a constant as was suggested by Sommerfeld.† This fact will solve the difficulty of Sommerfeld's theory, in which it is necessary to use mixed numbers, or negative numbers, instead of whole positive integers, to get agreement with experiments.

(2) Under the same distribution of electrons in an atom, the calculated values $\Delta\nu_H$ should be larger in the case of the radiation which takes place in the region having more electrons outside.

We obtained calculated values of $\Delta\nu_H$ for the formula (3). In this calculation the wave number differences between $L\alpha_2$ and $L\beta_1$ are substituted for $\Delta\nu$ successively, and $l = 3\cdot63$ is given for the numerical value of l. Now,

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[*] L. Vegard, 'Phil. Mag.,' vol. 35, p. 293 (1918).

[†] A. Sommerfeld, 'Ann. der Physk.,' vol. 51, p. 127 (1916).

inversely, let us give the observed values to $\Delta\nu$ and $\Delta\nu_H$ in the expression (3), and find the real values of l which will give the numerical value 0·365 to the corresponding expressions of hydrogen doublets.

If l be such values, it will be expressed—

$$\frac{\Delta\nu}{(Z-l)^4}=0\cdot365\left\{1+\frac{5}{2}\frac{\alpha_2}{2^2}(Z-l)^2+\frac{53}{8}\frac{\alpha^4}{2^4}(Z-l)^4+\dots\right\}\qquad(4)$$

The difference between l and 3·63 being very small, we can put $l=3\cdot63$, as the first approximation, for the higher terms of the relativity correction.

Then we have:

$$1+\frac{5}{2}\frac{\alpha^2}{2^2}(Z-l)^2+\frac{53}{8}\frac{\alpha^4}{2^4}(Z-l)^4+\dots$$

$$\fallingdotseq 1+\frac{5}{2}\frac{\alpha^2}{2^2}(Z-3\cdot63)^2+\frac{53}{8}\frac{\alpha^4}{2^4}(Z-3\cdot63)^4+\dots\dots\dots\qquad(5)$$

From (4) and (5) the values of l can be obtained as shown in Table IV.

Table IV.

Numerical Values of l.			Numerical Values of l.		
Atomic Number.		l	Atomic Number.		l
41	Nb	3·42	65	Tb	3·54
44	Ru	3·93	66	Dy	3·50
47	Ag	3·36	71	Lu	3·08
48	Cd	3·41	73	Ta	3·11
49	In	3·44	74	W	3·16
50	Sn	3·60	78	Pt	3·17
53	J	3·42	79	Ag	3·16
56	Ba	3·56	83	Bi	2·98
57	La	3·63	90	Th	2·68
58	Ce	3·66	92	U	2·67
59	Pr	3·51			

According to Table III and Table IV the change of numerical values of the $\Delta\nu_H$, consequently l, is clearly systematic in the elements of the large atomic numbers; in the elements of the smaller atomic numbers we cannot find any systematic changes. It will probably, I think, be due to the difference of the distances between the orbits. To get fuller conclusions about it, it would be necessary to obtain more accurate experimental data concerning the wavelengths of X-rays of the light elements.

The radiation of the K usually taking place at a part of the atom nearer to the centre than that of the L series, it is quite possible from the previous conclusion (2) that: (*a*) the value of $\Delta\nu/(Z-3{\cdot}63)^4$ (which we wrote in Table II as $\Delta\nu/(Z-l)^4$ is usually greater in the K series than in the L series for the same element; (*b*) that in the same series, these values are greater in the elements of higher atomic numbers than in those of smaller atomic numbers, and this difference due to the atomic number should be more noticeable in the L series than in the K series.

There might possibly be some exceptions, because the values of the effective nuclear charge should be affected by the distances from the neighbouring orbits.

§ 3°. *On the O Term of X-Ray Radiation.*

Coster noticed that besides L doublets, the wave-length differences between the lines β_2—β_5, γ_1—γ_6, γ_2—γ_3, β_4—β_3, β_2—β_8, β_2—β_7, remain the same for all elements.

From the direct consequence of the fact above stated, it is remarkable that the differences of the wave-lengths between β_7—β_5 and β_8—β_7, etc., remain constant throughout the whole of the elements. These differences are shown in Table V.

Let us consider, generally, the case that an electron is thrown out from one of its stationary orbits with the quantum number M, to another stationary orbit with the quantum number N; then it suddenly radiates out the difference of the energies in the two orbits in the form of a monochromatic wave. In such a case, if we adopt Sommerfeld's idea of elliptic orbits, then the wave number ν of the monochromatic wave should be expressed by

$$\nu = (n\,.\,n') - m\,.\,m') \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where

$$(n\,.\,n') = \mathrm{N}\left(\frac{\mathrm{E}}{2}\right)^2\left\{\frac{1}{(n\,.\,n')^2} + \frac{a^2}{(n+n')^4}\left(\frac{\mathrm{E}}{e}\right)^2\left(\frac{1}{4}+\frac{n'}{n}\right) + \ldots\right\} \qquad (6a)$$

n, n'; the azimuth and radial quantum numbers of the final orbits and m, m' are those of the initial orbits.

and

$$\left.\begin{aligned} \mathrm{M} &= m + m' \\ \mathrm{N} &= n + n' \end{aligned}\right\} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

The stationary orbits of the quantum number M consists of M elliptic orbits of different eccentricity. With respect to the stationary orbits of the quantum number N the above holds also in this case and they consist of N different elliptic orbits.

Table V.

Atomic Number.		Differences of the wave-lengths.		Differences of the wave-number.		Ratio.	Differences of wave-lengths.	Differences of wave-number.
		$\beta_7-\beta_5$	$\beta_8-\beta_7$	$\beta_5-\beta_7$	$\beta_7-\beta_8$		$\gamma_7-\gamma_6$	$\gamma_6-\gamma_7$
73	Ta	9·4	13·8	5·35	7·70	3·43	—	—
74	W	8·3	14·6	5·11	9·15	3·53	6·8	4·90
76	Os	—	—	—	—	—	—	—
77	W	—	—	—	—	—	—	—
78	Pt	8·4	14·3	6·64	11·03	3·51	—	—
79	Au	8·3	14·4	6·93	11·83	3·51	—	—
81	Tl	9·7	—	8·83	(13·92)	3·49	—	—
82	Pb	9·48	14·5	9·51	14·19	3·45	—	—
83	Bi	—	—	—	—	—	—	—
90	Th	—	—	—	—	—	—	—
92	U	11·87	—	20·29	—	—	—	—

Now suppose that quantum number of the initial orbits M be 5 and that of the final orbits N be 2. Then there must exist 5 initial orbits and 2 final orbits.

For the sake of convenience we shall name these orbits in the order of their eccentricities as 1st final orbit, 2nd final orbit and 1st. initial orbit, 2nd initial orbit, 3rd initial orbit, etc., respectively.

In this case the expressions (7) become

$$\left.\begin{aligned} N &= n + n' = 2 \\ M &= m + m' = 5 \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7a)$$

The radiations are emitted when an electron passes from one of the initial orbits to one of the final orbits. Therefore we should have two sets of quintets; one caused by the falling of an electron from 5 different initial orbits to one of the final orbits, and the other formed by combining the 5 initial orbits with the remaining final orbit. Thus the wave numbers of the components of one of the quintets are:

$$\left.\begin{aligned} \nu_{1-1} &= (2.0) - (5.0) \\ \nu_{1-2} &= (2.0) - (4.1) \\ \nu_{1-3} &= (2.0) - (3.2) \\ \nu_{1-4} &= (2.0) - (2.3) \\ \nu_{1-5} &= (2.0) - (1.4) \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

and those of the other set of quintets are:

$$\left.\begin{aligned} \nu_{2-1} &= (1.1) - (5.0) \\ \nu_{2-2} &= (1.1) - (4.1) \\ \nu_{2-3} &= (1.1) - (3.2) \\ \nu_{2-4} &= (1.1) - (2.3) \\ \nu_{2-5} &= (1.1) - (1.4) \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

where ν_{s-t} means the wave number of the radiation emitted by the transition of an electron from t^{th} initial orbit to s^{th} final orbit.

It will easily be seen from (8) and (9) that the wave number differences between any two corresponding numbers of the two sets of quintets must be the same, as shown by the following relation :—

$$\left.\begin{aligned}&\nu_{2-1}-\nu_{1-1}\equiv\nu_{2-2}-\nu_{1-2}\equiv\nu_{2-3}-\nu_{1-3}\\&\equiv\nu_{2-4}-\nu_{1-4}\equiv\nu_{2-5}-\nu_{1-5}\equiv(1.1)-(2.0)\end{aligned}\right\}\cdots\cdots\cdots\cdots\cdots\ (10)$$

By (8) and (9) the wave number differences between two successive components of a quintet should be expressed by :—

$$\left.\begin{aligned}\Delta\nu_1&=\nu_{1-2}-\nu_{1-1}=\nu_{2-2}-\nu_{2-1}=(4.1)-(5.0)\\\Delta\nu_2&=\nu_{1-3}-\nu_{1-2}=\nu_{2-3}-\nu_{2-2}=(3.2)-(4.1)\\\Delta\nu_3&=\nu_{1-4}-\nu_{1-3}=\nu_{2-4}-\nu_{2-3}=(2.3)-(3.2)\\\Delta\nu_4&=\nu_{1-5}-\nu_{1-4}=\nu_{2-5}-\nu_{2-4}=(1.4)-(2.3)\end{aligned}\right\}\cdots\cdots\ (11)$$

According to Sommerfeld the intensities of their components are :—

$$\left.\begin{aligned}J_{1-1}&=\frac{2}{2}\cdot\frac{5}{5}=1\\J_{1-2}&=\frac{2}{2}\cdot\frac{4}{5}=\frac{4}{5}\\J_{1-3}&=\frac{2}{2}\cdot\frac{3}{5}=\frac{3}{5}\\J_{1-4}&=\frac{2}{2}\cdot\frac{2}{5}=\frac{2}{5}\\J_{1-5}&=\frac{2}{2}\cdot\frac{1}{5}=\frac{1}{5}\\J_{2-1}&=\frac{1}{2}\cdot\frac{5}{5}=\frac{1}{2}\\J_{2-2}&=\frac{1}{2}\cdot\frac{4}{5}=\frac{2}{5}\\J_{2-3}&=\frac{1}{2}\cdot\frac{3}{5}=\frac{3}{10}\\J_{2-4}&=\frac{1}{2}\cdot\frac{2}{5}=\frac{1}{5}\\J_{2-5}&=\frac{1}{2}\cdot\frac{3}{5}=\frac{1}{10}\end{aligned}\right\}\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\ (12)$$

Where $J_{s\text{-}t}$ means the intensity of the radiation emitted by the transition of and electron from t^{th} initial orbit to s^{th} final orbit.

All the above propositions can be applied in the case of X-ray radiations by interchanging 'the nuclear E/e in the formulæ (8), (9), 10), (11) and (12) with the effective nuclear charges.

If we consider K, L, M, N, O, P, --- orbits as the stable orbits in an atom, then K, L, M, N, O, P, · · · terms should have the quantum numbers 1, 2, 3, 4, 5, 6 · · · respectively. Now let o be the correction applied to the O term for nuclear charge due to the effect of the other electrons in the atom then $(Z - o)e$ should be the effective nuclear charge for this term. Thus for the quintets due to the O term, the wave-number differences between their components can be obtained by putting the total effective nuclear charge E equal to $(Z - o)e$ in (11) and (12).

$$\left.\begin{aligned}
\Delta\nu_1 &\doteq \frac{N\alpha^2}{5^4}\frac{1}{4}(Z - o)^4 \\
\Delta\nu_2 &\doteq \frac{N\alpha^2}{5^4}\frac{5}{12}(Z - o)^4 \\
\Delta\nu_3 &\doteq \frac{N\alpha^2}{5^4}\frac{5}{6}(Z - o)^4 \\
\Delta\nu_4 &\doteq \frac{N\alpha^2}{5^4}\frac{5}{2}(Z - o)^4
\end{aligned}\right\} \qquad (13)$$

Therefore

$$\Delta\nu_1 : \Delta\nu_2 : \Delta\nu_3 : \Delta\nu_4 = 3 : 5 : 10 : 30. \qquad (14)$$

The differences between the wave numbers of the lines and the ratio between them are shown in Table V. Actually it is very remarkable that for all the elements examined the ratio of the wave number differences between $\beta_5 - \beta_7$, and $\beta_7 - \beta_8$ always remains the same as the ratio between $\Delta\nu_1 : \Delta\nu_2$ in (14) and equal to $3 : 5$ within the limit of the experimental errors.

In the case of tungsten, the line γ_6 which forms a doublet with β_5 accompanies a feeble line γ_7, and the difference of the wave-numbers between them is equal to that of between β_5 and β_7.

Thus it seems to be legitimate to consider that the lines $L\beta_5$, $L\beta_7$, $L\beta_8$ belong to one of the two sets of quintets, and that $L\gamma_6$ and $L\gamma_7$ belong to the other set of quintets, each component of these quintets being generated by the falling of an electron from one of the O orbits to one of the L orbits. The wave number of these lines will be represented by

$$\left.\begin{array}{ll} L\beta_5 & \nu = L_1 - O_1 \\ L\beta_7 & \nu = L_1 - O_2 \\ L\beta_8 & \nu = L_1 - O_3 \\ L\gamma_6 & \nu = L_2 - O_1 \\ L\gamma_7 & \nu = L_2 - O_2 \end{array}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

Where $L_1 - O_1$, $L_1 - O_2$, and $L_1 - O_3$ are the wave numbers of the radiation emitted by an electron which comes to the L_1 orbit from the O_1, O_2 and O_3 orbits respectively and $L_2 - O_1$, and $L_2 - O_2$ the wave numbers corresponding to a drop between the L_2 orbits and O_1, O_2 orbits respectively. O_1, O_2, O_3, O_4, O_5 are corresponding terms of 1st, 2nd, 3rd, 4th and 5th orbits of the quintet. The absence of the lines having initial orbits O_4, O_5 can be explained by the intensity law (12). According to (12) they should be very feeble lines.

Now adopting the theory of quintets and replacing the nuclear charge by the effective charge, we get the following values for Os :—

$$\left.\begin{array}{l} O_1 = (5.0)_{E=(Z-o)e} \doteq N(Z-o)^2\left\{\frac{1}{5^2} + \frac{1}{4}\frac{\alpha^2}{5^2}(Z-o)^2\right\} \\ O_2 = (4.1)_{E=(Z-o)e} \doteq N(Z-o)^2\left\{\frac{1}{5^2} + \frac{1}{2}\frac{\alpha^2}{5^4}(Z-o)^2\right\} \\ O_3 = (3.2)_{E=(Z-o)e} \doteq N(Z-o)^2\left\{\frac{1}{5^2} + \frac{11}{12}\frac{\alpha^2}{5^4}(Z-o)^2\right\} \\ O_4 = (2.3)_{E=(Z-o)e} \doteq N(Z-o)^2\left\{\frac{1}{5^2} + \frac{7}{4}\frac{\alpha^2}{5^4}(Z-o)^2\right\} \\ O_5 = (1.4)_{E=(Z-o)e} \doteq N(Z-o)^2\left\{\frac{1}{5^2} + \frac{17}{4}\frac{\alpha^2}{5^4}(Z-o)^2\right\} \end{array}\right\} \quad (16)$$

o being the correction term for nuclear charge due to other electrons, it seems quite reasonable that o remains nearly constant for the elements which belong to the same row of the periodic system.

Employing the calculated values of l in Table IV, the numerical values of the L_1 and L_2 terms for any element are obtained by the following formulæ given by Sommerfeld :—

$$L_1 = (2.0) = N(Z-l)^2\left\{\frac{1}{2^2} + \frac{1}{4}\frac{\alpha^2}{2^4}(Z-l)^2 + \frac{1}{8}\frac{\alpha^4}{2^6}(Z-l)^4 + \frac{5}{64}\frac{\alpha^6}{2^8}(Z-l)^6 + \ldots\right\},$$

$$L_2 = (1.1) = N(Z-l)^2\left\{\frac{1}{2^2} + \frac{5}{4}\frac{\alpha^2}{2^4}(Z-l)^2 + \frac{21}{8}\frac{\alpha^4}{2^6}(Z-l)^4 + \frac{429}{64}\frac{\alpha^6}{2^8}(Z-l)^6 + \ldots\right\},$$

From the numerical values of the wave numbers of each line and the numerical values of L_1 and L_2 thus obtained, we can calculate by (15) the numerical values of O_1, O_2, O_3.

Consequently, the numerical values of o can be obtained by (16), which are shown in Tables VI, VII, VIII, IX and X.

Table VI.

Atomic Numbers.		$\nu\beta_5/N.$	$L_1/N.$	$O_1/N.$	$(Z - o)^2$	$Z - o$	o
73	Ta	728·65	1241·16	512·51	12724	113	− 40
74	W	751·56	1275·47	523·91	13007	114	− 40
78	Pt	851·57	1426·28	574·71	14254	120	− 42
79	Au	877·70	1465·68	587·78	14582	121	− 42
83	Bi	987·98	1634·50	646·52	16019	126	− 43
90	Th	1194·94	1955·75	760·81	18832	137	− 47
92	U	1258·43	2049·35	790·92	19558	140	− 48

Table VII.

Atomic Numbers.		$\nu\beta_7/N.$	$L_1/N.$	$O_2/N.$	$(Z - o)^2$	$Z - o$	o
73	Ta	723·30	1241·16	517·86	12781	113	− 40
74	W	746·45	1275·47	529·02	13056	114	− 40
78	Pt	844·93	1426·28	581·35	14347	120	− 42
79	Au	870·77	1465·68	594·91	14668	121	− 42
92	U	1238·14	2049·35	811·21	19921	141	− 49

Table VIII.

Atomic Numbers.		$\nu\beta_8/N.$	$L_1/N.$	$O_3/N.$	$(Z - o)^2$	$Z - o$	o
73	Ta	715·60	1241·16	526·16	12934	114	− 41
74	W	737·60	1275·47	537·87	13222	115	− 41
78	Pt	833·90	1426·28	592·38	14534	120	− 42
79	Au	858·94	1465·68	607·74	14896	122	− 43
82	Pb	936·03	—	—	—	—	—
83	Bi	—	1634·50	—	—	—	—
90	Th	—	1955·75	—	—	—	—
92	U	—	2020·49	—	—	—	—

Table IX.

Atomic Numbers.		$\nu\beta_5$/N.	L_3/N.	O_1/N.	$(Z-o)^2$	$Z-o$	o
73	Ta	820·98	1331·03	510·05	12662	113	− 40
74	W	850·08	1371·12	521·04	12935	114	− 40
78	Pt	978·07	1546·70	568·63	14103	119	− 41
79	Au	1011·12	1592·68	581·56	14424	120	− 41
83	Bi	1149·20	1796·47	647·27	16038	126	− 43
90	Th	—	2191·40	—	—	—	—
92	U	1507·82	2303·82	796·00	19674	140	− 48

Table X.

Atomic Numbers.		$\nu\beta_7$/N.	L_3/N.	O_2/N.	$(Z-o)^2$	$Z-o$	o
74	W	1371·12	1371·12	525·94	12980	114	− 40

It will be clear from these tables that the values of o, calculated in such a way, agree fairly well with each other for each element separately.

§ 4°. *On the initial and final stationary Orbits corresponding to X-ray Radiation.*

We have stated that the wave-length differences between the lines $L\beta_3$ and $L\beta_4$ are constant throughout all the elements.

The wave-length differences between the lines $L\gamma_3$ and $L\gamma_4$ are also nearly constant throughout all the elements. And these two pairs are looked upon by Sommerfeld as differing essentially from the five pairs of L doublets described before. These two doublets were once called the λ doublets by him. But strictly speaking the wave-length differences between γ_4—γ_3 are not constant throughout all the elements, and moreover the wave-number differences of the two doublets above mentioned are not the same for the same element. On the contrary, the wave-length difference between β_3 and β_4 is constant throughout all the elements. Thus, let us consider the pair of lines β_3 and β_4 only, as the λ doublet, which are produced by electrons falling from the M_3 and M_4 orbits down to the L_3 orbit respectively.

According to de Broglie,* Hertz,† Duane and Patterson‡ there are one, three and five absorption edges in the regions of the K, L and M series respectively. Let L_1, L_2, L_3, M_1, M_2, M_3, etc., be the stationary orbits counted from the outside of the atom corresponding to the absorption edges in the regions of the L and M series respectively. These L_1, L_2 and M_1, M_2 are considered to be the same as those denoted by the same symbols in the case of radiation. Thus, the absorption edges can be named by the names of the stationary orbits corresponding to them.

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* M. De Broglie, 'C.R.,' vol. 158, p. 1,493 (1914).

† G. Hertz, 'Z. f. Physik,' vol. 3, p. 19 (1920).

‡ Duane and R. A. Patterson, 'Poc. Nat. Acad. Sci.,' Washington, Sept., 1920.

As is noticed by Duane,*† Smekal‡ and others, the wave number differences corresponding to some combinations of the orbits coincide with those of certain lines belonging to K, L and M series. This relation can easily be extended to the whole region of X-ray spectra from the already known facts (*i.e.*, the facts concerning K doublet, L doublets, quintets, and λ doublet), by appropriate calculations combining the numerical values of the wave-numbers corresponding to the absorption edges and those of the emitted lines. For the sake of brevity let us omit the details of the calculations; but we can determine the initial and final orbits of electrons to produce the X-ray spectra, which are mentioned in the following table:—

Table XI.—The initial and final orbits of electrons in X-ray Radiations.

Radiation.	Initial Orbit.	Final Orbit.	Radiation.	Initial Orbit.	Final Orbit.	Radiation.	Initial Orbit.	Final Orbit.
$K\alpha_3$	L_3	K	$L\gamma_4$	O′	L_3	$L\beta_7$	O_2	L_1
$K\alpha_2$	L_2	K	Ll	O_5	L_1	$L\beta_5$	O_1	L_1
$K\alpha_1$	L_1	K	$L\eta$	M_5	L_1	$L\gamma_7$	O_2	L_2
$K\beta_3$	M_4	K	$L\alpha_2$	M_2	L_1	$L\gamma_6$	O_1	L_2
$K\beta_1$	M_3	K	$L\beta_1$	M_2	L_2	$M\alpha_1$	N_1	M_1
$K\beta_2$	N_6	K	$L\beta_6$	N_7	L_1	$M\alpha_2$	N_2	M_1
$K\gamma$	N_5	K	—	—	—	—	—	—
$L\beta_4$	M_4	L_2	$L\gamma_5$	N_1	L_2	M	N_2	M_2
$L\beta_3$	M_3	L_2	$L\beta_2$	N_3	L_1	$M\beta$	N_3	M_2
$L\gamma_2$	N_6	L_3	$L\gamma_1$	N_4	L_2	$M\epsilon$	N_4	M_4
$L\gamma_3$	N_5'	L_2	$L\beta_8$	O_3	L_1	$M\delta$	O_1	M_2

By these above arithmetical operations the wave number of all the orbits can be directly found, except that of the O′ orbit.

With regard to the line $L\gamma_4$ which is produced by the electrons falling down to L_3 orbit, we can get the following numerical values of the wave numbers from Table I.

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* W. Duane and T. Shimizu, 'Phys. Rev.,' vol. 14, p. 73 (1919).

† W. Duane and W. Stenstrom, 'Phys. Rev.,' vol. 15, p. 328 (1920).

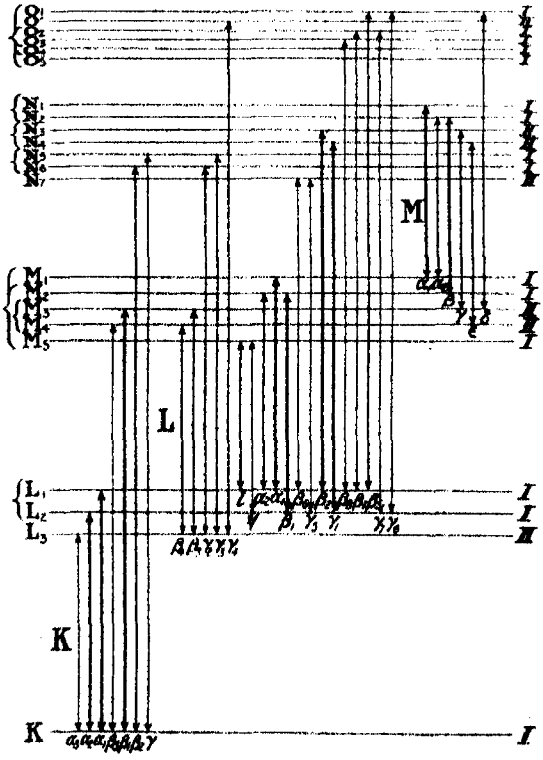
‡ A. Smekal, 'Z. f. Physik,' vol. 5, p. 121 (1921).

Table XII.

Atomic Number.		β_5	$\gamma_4-(L_3-L_1)$	β_7
73	Ta	723·30	728·65	728·65
74	W	746·45	748·70	751·56
79	Au	870·77	870·72	877·70
82	Pb	950·22	954·57	959·72

According to Table XI, the initial and final orbits of the lines $L\beta_5$ and $L\beta_7$ are O_1, L_1 and O_2, L_2 respectively; and those of the line $L\gamma_4$ are O' and L_3. Thus, if we arrange the orbits in order of their wave numbers, the initial orbit of $L\gamma_4$ or O' orbit should be situated between the O_1 and O_2 orbits.

The facts stated in this chapter regarding the initial and final orbits of the lines are expressed in the accompanying figure. In this diagram the stationary orbits are arranged in order of decreasing wave numbers from the bottom.



§ 5°. *On the Planes of the stationary Orbits.*

In an atom which has only one electron in it as in the case of hydrogen, ionized helium, etc., the state of the electron is determined by two conditions: *e.g.*, the distances from the nucleus to the electron and the azimuth angle of the electron on the stationary orbit measured from the perihelion or aphelion of the stationary orbit.

On the other hand, in the case of an element of large atomic weight and consequently having many electrons in its atom, the validity of the above consideration is very doubtful. In such a case, let us assume that the stationary orbit of every electron is not necessarily always situated on the same plane. Then to determine the state of every electron on the stationary orbit, one more co-ordinate is needed, besides the two co-ordinates above stated, to determine the inclination of the orbital plane. In short, three co-ordinates should be needed in such a case. Consequently as was considered by Smekal,* besides radial and azimuth quantum numbers n, n', let us consider a spatial quantum number n'', where n never equals zero as in the case previously considered.

Now, let us use the expression (n, n', n'') for the quantum numbers of a stationary orbit having radial, azimuth, and spatial quantum numbers n, n', n'' respectively.

Considering the quantum numbers of the K, L, M, N, and O orbits to be 1, 2, 3, 4 and 5 respectively as before, and let us take all possible cases. Then, the K, L, M, N and O orbits should consist of the stationary orbits having the quantum numbers shown in the left side of the column in Table XIII.

For the sake of abbreviation let us define that the stationary orbits, which fulfil the condition that the spatial quantum number n'' and the sum of the azimuth and radial quantum numbers $n + n'$ remain equal for every one of these orbits, are in the fine-structure relation.

Then, according to the facts stated in our foregoing arguments, the following six sets of the stationary orbits are in the fine-structure relation, viz., L_1 and L_2, M_1, M_2 and M_5, M_3 and M_4, N_1, N_2, N_3 and N_4, N_5 and N_6, O_1, O_2, O_3, O_4 and O_5.

The difference of the ratio between the quantum numbers of the stationary orbit $n''/n + n''$ means the difference of the orbital planes of the stationary orbit. Thus, we can classify the stationary orbits into many groups according to their orbital planes by aid of their spatial quantum numbers n''.

Now, let us call the group of the stationary orbits on the plane represented

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* A. Smekal, 'Z. f. Physik,' vol. 4, p. 21 (1921).

Table XIII.—The possible Quantum Numbers of the Stationary Orbits.

Case $n'' = 0$	Case $n'' = 1$	Case $n'' = 2$	Case $n'' = 3$	Case $n'' = 4$
K series (1, 0, 0) K	—	—	—	—
$n + n' + n'' = 1$				
L Series (2, 0, 0) L_1	(1, 0, 1) L_3	—	—	—
$n + n' + n'' = 2$				
(1, 1, 0) L_2				
M Series (3, 0, 0) M_1	(2, 0, 1) M_3	(1, 0, 2)	—	—
$n + n' + n'' = 3$				
(2, 1, 0) M_2	(1, 1, 1) M_4	—	—	—
(1, 2, 0) M_5	—	—	—	—
N Series (4, 0, 0) N_1	(3, 0, 1) N_3	(2, 0, 2)	(1, 0, 3)	—
$n + n' + n'' = 4$				
(3, 1, 0) N_2	(2, 1, 1) N_4	(1, 1, 2)	—	—
(2, 2, 0) N_5	(1, 2, 1) N_7	—	—	—
(1, 3, 0) N_6	—	—	—	—
O Series (5, 0, 0) O_1	(4, 0, 1) O′	(3, 0, 2)	(2, 0, 3)	(1, 0, 4)
$n + n' + n'' = 5$				
(4, 1, 0) O_2	(3, 1, 1)	(2, 1, 2)	(1, 1, 3)	—
(3, 2, 0) O_3	(2, 2, 1)	(1, 2, 2)	—	—
(2, 3, 0) O_4	(1, 3, 1)	—	—	—
(1, 4, 0) O_5	—	—	—	—

by the condition $n'' = 0$, the I group, etc. Then, according to Table XIII every orbit consists of a certain number of the stationary orbits, as in the following :—

K orbit : one stationary orbit of group I.
L orbit : two stationary orbits of group I.
one stationary orbit of group II.
M orbit : three stationary orbits of group I.
two stationary orbits of group II.
O orbit : five stationary orbits of group I.
four stationary orbits of group II.

As for the group I, let us take the following lines :—

$K, L_1, L_2, M_1, M_2, M_5, N_1, N_2, N_5, N_6, O_1, O_2, O_3, O_4, O_5$.

and as for the group II :

$L_3, M_3, M_4, N_3, N_4, N_7$, O′.

The signs I, II on the right side of the orbits in the diagram given above, express the groups to which they belong.

Referring to the results of the previous considerations, we can find the correspondence between each stationary orbit and its three quantum numbers n, n', n''. The right side of the columns of Table XIII shows the names of the stationary orbits corresponding to the quantum numbers in the left side.

It is very obvious from the definition of the fine-structure relation that only the stationary orbits which belong to the same group are in the fine-structure relation, *e.g.*, L and λ doublets, triplets, quadruplets, quintets, etc., in which the wave-length differences are equal throughout all the elements, are generated by the differences of eccentricities (except the case of λ doublet) of the stable orbits in the same plane.

The sign } between some stationary orbits in the diagram given above shows that the stationary orbits connected by it are in the fine-structure relation.

The ratio of the wave-number differences corresponding to some stable orbits connected by } does not necessarily take the numerical values given by Sommerfeld. For example, the ratio of the wave-number differences between M_1—M_2 and M_2—M_5 is not equal to 1·3 as theoretically given by Sommerfeld. It may probably be due to the electrons on the stationary orbits belonging to another plane passing through between the stationary orbits, which are responsible for the formation of the fine-structure relation, and that the effective nuclear charge changes in some of the latter stationary orbits by the influence of the electrons revolving on the former stationary orbits.

Now, examining every line in the diagram, we arrive at the following conclusion :—

(1) In every radiation caused by the transition of the electrons between two successive orbits as from L to K, and M to L, the initial and final stationary orbits belong to the same group.

(2) In every radiation caused by the transition of the electrons from the outer orbit to the inner orbit passing though an odd number of intermediate orbits, as from M to K, from N to L, and from O to K, the initial and final orbits belong to the different group; but if the transition takes place by passing through an even number of intermediate orbits, as from K to N, and from L to O, the initial and final orbits belong to the same group.

In short, the electron moves from a certain outer orbit to the neighbouring inner one without changing its spatial quantum number, but if there are some intermediate orbits between the initial and final orbit, the electron changes its spatial quantum number every time it passes through one of the intermediate orbits.

These conclusions also give physical basis to Coster's *a-b* law in certain respects.* The only difficulty in our conclusions is that there is an exception with regard to a feeble line $K\alpha_3$ observed by Duane and Stenstrom,† the initial and final stationary orbits are L_3 and K respectively.

In conclusion, the sincere thanks of the author are due to Professor Sir W. H. Bragg, Professor J. W. Nicholson, and Dr. G. B. Jeffery, for their kind advice on my work. Also, I wish to express my indebtedness to U. Yoshida, whose research on X-ray analysis of mica crystals was useful to me on many occasions.

The Absolute Energies of the Groups in Magnetic β-Ray Spectra.

By C. D. Ellis, Ph.D., Fellow of Trinity College, Cambridge, and H. W. B. Skinner, B.A., Coutts-Trotter Student of Trinity College, Cambridge.

(Communicated by Prof. Sir E. Rutherford, F.R.S.—Received November 21, 1923.)

Most β-ray bodies emit several homogeneous groups of β-rays, and the energies of the electrons forming these groups may be found from the deflection they suffer in a magnetic field. Various experiments have shown that these groups are due to the conversion, according to the quantum relation, of γ-rays in the different electronic levels of the atom. In fact, the energy of any group is of the form

$$E_1 = h\nu - (\text{absorption energy of level}).$$

Two β-ray groups due to the conversion of a γ-ray of definite frequency in the K and L levels of the atom will differ in energy by the difference in energy between the K and L absorption energies. Both in testing this equation, and in using it to deduce frequencies of the γ-rays, it is necessary to compare energies of β-rays determined in terms of a magnetic field, with absorption energies deduced from wave-length measurements of X-rays. It is thus important to obtain values of the absolute β-ray energies as accurate as possible. The most accurate previous values were those of Rutherford and Robinson.‡

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* D. Coster, 'Z. f. Physik,' vol. 6, p. 202 (1921).

† W. Duane and W. Stenstrom, 'Phys. Rev.,' vol. 15, p. 328 (1920).

‡ 'Phil. Mag.,' vol. 26, p. 717 (1913).

The relative energies of β-ray lines from different bodies can be easily measured, and so to fix the scale of all β-ray lines it is only necessary to determine the absolute energies of certain strong lines from one body. Radium B was the most convenient body to use, and we have measured the Hρ's of six of the stronger lines to an accuracy of at least 1 in 500, and possibly better, while the accuracy of the corresponding energies is somewhat lower.

Having once measured these lines the Hρ values of any other line can be measured with practically equal accuracy. All that is necessary is to use a uniform magnetic field and to take a photograph, so that the line in question appears on the same plate as one of the standard lines. The Hρ's are then simply in the ratio of the ρ's. Where the Hρ's differ too much for them to be compared directly an intermediate step-up line is used.

Our final results are given in § 7 at the end of the paper, and the intermediate paragraphs are concerned with the details of the measurement.

§ 2. *Method employed.*

The method used was to photograph β-ray lines by the usual focussing method, and to measure the magnetic field by a modified ballistic method in terms of the area-turns of a search coil and a mutual inductance.

The focussing method is illustrated in fig. 1.

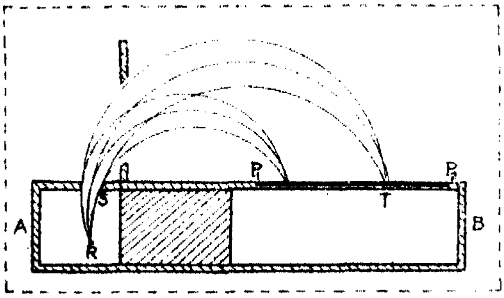

FIG. 1.

The apparatus AB is in an evacuated box between the poles of a large electromagnet. If the magnetic field is uniform and perpendicular to the paper, the β-particles emitted from the source R travel in circles, and it can be seen that those in a comparatively wide solid angle, as determined by the slit S, focus on the photographic plate P_1P_2. The constant radius of curvature ρ of the β-particle in the uniform field is determined from the position of the trace T on the photographic plate relative to R; multiplication by H, the value of the magnetic field, as determined by the search coil, gives Hρ, and the energy is obtained from this by the usual relativity formulæ.

The general method of measuring the magnetic field at a given point is described in § 3. The measurements on the search coil are given in § 4. To obtain the actual field which deflects the β-rays it is necessary to know the uniformity of the field over the path. This point is discussed in § 5. Since it was found that for the same current in the field coils the magnetic field did not repeat itself exactly, it was necessary to measure the actual field in each experiment. This is discussed in § 6.

To complete the measurement we need to know ρ, the radius of curvature of the β-particles. This is obtained by measuring up the plate and apparatus, and the method and corrections are given in § 7.

§ 3. *Measurement of the Magnetic Field.*

The magnetic fields to be measured were of the order of 300 Gauss. They were determined by comparing by a balance method the total change in induction on turning the search coil through 180° in the magnetic field with that due to breaking the primary current in a mutual inductance.

The search coil was mounted on a long brass tube in bearings as shown in fig. 2.

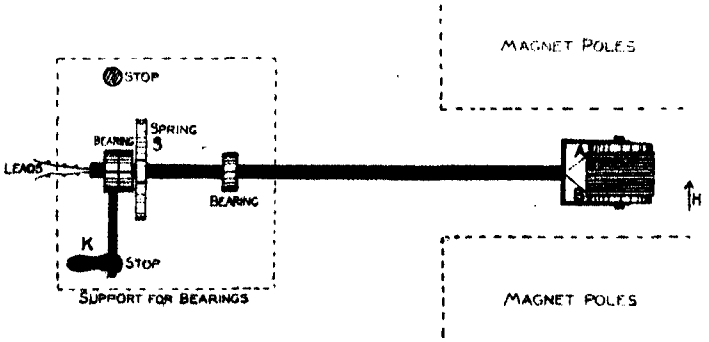

FIG. 2.

The coil could be rotated through 180°, the handle K moving between fixed stops. The actual angle turned through by the coil was found to be within 2′ of 180°. A catch held the coil against one of the stops, and on releasing the catch a spiral spring at S rotated the coil sharply to the other position. The leads from the coil were taken out through the brass tube and connected in series with the secondary of the mutual inductance and a Grassot fluxmeter, the latter being used with lamp and scale. Instead of measuring first the throw due to reversing the coil and then that due to breaking the current in the primary of the inductance, it was found possible to use a balance method by doing both these operations at the same time and opposing the effects. The timing device consisted simply of a falling weight operating relays.

Owing to the difference in the shape of the two E.M.F. curves it was impossible to obtain a complete balance during the whole time of the rotation. The current surged first in one direction and then in the other, but the final shift of the fluxmeter spot showed accurately the net transfer. On account of the long period of the fluxmeter it was possible by careful timing to reduce the movement of the spot of light during the rotation to a very small amount.

The current in the primary of the mutual inductance which on being broken balanced the effect due to the rotation of the search coil was thus determined. This current was measured by finding the voltage drop across a standard resistance with a Tinsley potentiometer. The resistance was compared with a 1-ohm standard which was sent to the National Physical Laboratory for standardisation during the course of the work. The calibration of the potentiometer was also checked.

To the order of accuracy of the experiment it is clear that there is no error in the measurement of the absolute value of the current, and the error in determining the current for balance depends purely on the accuracy of balance. The latter was found by experiment to be about 1 part in 3,000. Another check on the accuracy of the measurement was provided as follows: Two mutual inductances were used in the work, and the ratio between their values was found by comparing the current in them necessary to balance the same magnetic field. One inductance was not quite constant in its value; it had only been made a short time, and the wire was wound on paraffined wood. We found the ratio changed slightly with time (1 in 300 in three weeks), but all the points lay smoothly on a curve. The ratio of the separate values as determined at the N.P.L. agreed with the interpolated value to 1 in 3,000.

To deduce the actual field for a given position of the search coil two other determinations are necessary, the value of the inductance and the area-turns of the coil.

The inductances were measured at the N.P.L. and their values given to 1 in 10,000 with the last figure dropped, so that for our purposes no error occurs here.

§ 4. *Measurement of the Search Coil.*

The search coil consisted of 67 turns of No. 40-gauge silk-covered wire wound on a marble cylinder, 2·5 cms. diameter and 2·0 cms. long. The cylinder was ground very true, and the wire wound evenly on it under a constant tension. The diameter over the marble and over the wire was measured, at various diameters at both ends, by a Hilger comparometer reading to 0·0001 cm.

The marble cylinder appeared to be truly cylindrical to our accuracy, and to have a diameter of

$$2{\cdot}5000 \pm 0{\cdot}0002 \text{ cms.}$$

The measurement of the diameter over the wire could not be made so accurately and was not quite the same at all diameters, but the variations were quite small, and we took a mean diameter of

$$2{\cdot}5352 \pm 0{\cdot}0008 \text{ cms. at one end}$$
$$\text{and of } 2{\cdot}5374 \pm 0{\cdot}0010 \text{ cms. at the other.}$$

The effective diameter is the mean between the diameter over the wire and over the marble. The error in the wire measurement is thus halved, but owing to the slight uncertainty due to the silk covering we estimate the final error in the area turns as not greater than 1 in 1000. Our value for the area-turns is 333·6 sq. cms. In this value it was necessary to consider a possible error arising from the small triangle formed by the leads going from the end of the brass tube to the two ends A and B. Both by calculation and by measurement with compensation leads this effect was found to be less than 1 in 3000.

The susceptibility of the coil as a whole was tested for the presence of magnetic impurities. Our result will not be 1 part in 1000 in error so long as the average susceptibility is less than 10^{-4} and our measurement of the susceptibility showed it to be less than $0{\cdot}04 \times 10^{-4}$. This measurement consisted in the comparison of the motion of the coil when freely suspended in a non-uniform magnetic field with the motion of a solution of ferric chloride when similarly suspended.

The coil was set perpendicular to the lines of force at the point by finding the position which gave the maximum value for the inductance current. It was verified that there was no measurable effect on the value of the mutual inductance due to stray fields, due to external parts of the primary circuit. Our measurements suggested a very slight effect of 1 part in 4000.

Summing up, therefore, it appears that the value of the field at a point could be obtained in arbitrary units to about 1 in 3000; to translate this to absolute units it has to be multiplied by the area-turns of the search coil, which probably reduces the accuracy to 1 in 1000.

§ 5. *Uniformity of the Field.*

To obtain the effective field over the paths of the β-rays it was necessary to know the variation of the field from uniformity. By placing the coil in different positions we found that over the portion used there was no point differing from the mean by as much as 1 in 1000. Mr. D. R. Hartree, of St. John's College, kindly worked out for us the weight to be attached to these variations.* Variations at the source or at the photographic plate are unimportant, the important place being about the middle point of the track. In fact, the variations have to be weighted by a factor cos θ, where θ is the angle between the tangent to the track at the point and the line joining the source R to the trace T. Taking this into account it was found that the relative effect between the different ρ's was negligible, but that the value at the point measured was probably about 1 in 2000 below the effective value. Although this correction is just outside the limit of accuracy in the experiment it is included in the results.

§ 6. *Reproducibility of the Field.*

It was thought at first that it might be possible to calibrate the magnet in terms of the current in the field coils as measured on the potentiometer, but experiment showed that values of the field did not repeat themselves when we repeated the current. Various methods of establishing the field were tried; the best proved to be continual reversal, at the current finally employed. Forty reversals appeared to give a value constant to at least 1 in 300. Since this would have lowered our accuracy considerably, all the fields used in taking photographs were individually measured.†

Before a photograph was taken the search coil was adjusted in its standard position inside the brass box and the field measured. The coil was then removed and the β-ray apparatus introduced, the magnet field remaining switched on the whole time. During the interval between measuring the field and taking the photograph the current in the field coils usually dropped a few parts in a thousand. The field was corrected for this drop by direct subsidiary experiments. A slight hysteresis effect was distinctly noticeable. During the photograph the current was kept constant to a high order of accuracy.

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* 'Proc. Camb. Phil. Soc.,' p. 746 (1923).

† The use of air coils would have avoided this difficulty, but have introduced others due to the large currents that would have been necessary.

Finally we investigated the error which would be produced if any of the material of the β-ray apparatus were magnetic. We tested this as far as possible by measuring a field first when the apparatus was in the box, and secondly when it was not, and could detect no difference.

Summing up the last three paragraphs we conclude that the actual effective field occurring while the photograph was being taken could be measured to an accuracy of 1 in 1000.

§ 7. *Measurement of the Radius of Curvature.*

The method of obtaining the photograph has already been illustrated in fig. 1. The traces on the plate were sharply limited on the side further from the slit, and measurements were always taken to this place. The minimum radius of circles going through R and T is clearly $\frac{1}{2}$ RT and hence the further edge of the trace T given by a group of β-particles of definite velocity will be due to those β-particles which describe just a semi-circle before striking the plate, provided always that these particles are able to pass through the slit. The condition for this is that the foot of the perpendicular from the source to the plane of the plate should lie in the opening of the slit. This condition was always fulfilled in our apparatus. The radius of curvature required is thus $\frac{1}{2}$ RT.

The source of β-rays was radium B deposited on the surface of a platinum wire 0·024 cms. in diameter. Since the radius of curvature was about 6 cms. it is clear that errors would result unless the measurements were taken to the correct part of the source. The furthest portion of the trace will correspond to β-rays coming from that portion of the circumference of the source which is intersected by the line joining T to the centre of the source. It is inconvenient to measure to this point, so measurements were always taken to the highest point of the source (the plate being considered horizontal) and the correction was applied afterwards. It consisted in subtracting one quarter of the diameter of the source from ρ.

The question arises as to whether measurements can be made to this extreme edge of the trace. There are two considerations which are relevant, namely, the photographic spreading of the image and the systematic setting of the cross-wires inside the edge. For the first cause to give an error of 1 in 1000 it would be necessary for the spreading to amount to one-tenth of a millimetre and an examination of the plate under the microscope showed that the grains forming the image were nothing like this size. The second error mentioned might occur if the intensity of the line near the edge fell off slowly. That this is not the case and that the intensity falls off sharply and linearly can be seen from the photometer curves of β-ray lines published by Meitner.* A detailed calculation of the intensity distribution in a β-ray line made by Mr. Milne which will soon be published also brings out this point. Actually the plates were measured using a magnification of ten times, and even then the edge appeared quite definite, and we both agreed in our measurements of the same plate.

The trace as a whole is slightly curved concave towards the slit, but the furthest point is due to β-particles which travel perpendicular to the magnetic field. Measurements were always made to this point.

Before removing the plate from the apparatus a fiducial spot was photographed on to it, which fixed its position relative to the apparatus. The latter was then measured up with a travelling microscope having two motions at right angles. The plane of the plate was first adjusted parallel to the horizontal motion and the horizontal distance "1" between the source and the fiducial hole on the apparatus was measured. Then the plate was laid on the apparatus and the difference of height "d" between the film and the highest point of the source was found. The uncorrected ρ was calculated from the formula

$$4\rho^2 = d^2 + (1 - x)^2$$

where x is the distance of the edge of the line inside the fiducial spot. In these experiments "d" was about 1·45 cms. and $(1 - x)$ ranged from 9 to 14 cms.

The error in this uncorrected ρ was estimated as follows. Two marks were made on a piece of steel, and the distance between them calculated from their vertical and horizontal separation when the piece of steel was inclined. This calculated distance was compared with the distance as measured on a very accurate Hilger comparometer. The average error for the length we used was 0·004 cm. The actual measurements on the photographic plate agreed to 0·003 cm. Hence apart from the possibility of a systematic error in estimating the edge of the line, the actual error in the diameter of the circle the β-rays describe was probably less than 0·007 cm. The average diameter was 12 cms. (ρ = 6 cms.) so the final error in ρ should be anyway less than 1 in 1000.

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* 'Zeit. f. Physik,' vol. 11, p. 46 (1922).

§ 8. *Results.*

Our final results for Hρ are given in the table, together with the corresponding energies in volts calculated from the relativity formulæ. In calculating the energy the value $e/m = 1\cdot769 \times 10^7$ was used.*

H	Hρ					
156·8	661·0	768·9				
154·3	660·8	768·7				
269·7			1409·6	1675·8	1937·1	
312·1			1409·6	1675·1	1936·5	2256·0
336·9			1409·6	1675·6	1936·5	2255·2
365·9				1678·1	1939·6	2258·1
366·7				1678·0	1939·0	
Rounded final values Hρ	660·9	768·8	1410	1677	1938	2256
Energy in volts $\times 10^{-6}$	0·3725	0·4983	1·529	2·067	2·638	3·379

Previous Hρ values.

663	770	1392	1660	1925	2235†
660	766	1418	1690	1935	2242‡

It can be seen that the maximum deviation from the mean is less than 1 in 1000, which is in accordance with the discussion of the separate errors already given. We can conclude, therefore, that these figures are probably right to 1 in 1000 and should certainly be right to 1 in 500.

While the Hρ values of the first two lines are in good agreement with previous values, the four next are nearly 1 per cent. higher than the measurements of Rutherford and Robinson, and also differ, but in the opposite direction, from those of Danysz—that is to say, we find a markedly different ratio between the Hρ's of, for example, lines 1 and 3. This is a point which we could test independently of any measurements of the magnetic field. For if two lines can be obtained on the same plate in the same field, then since the field is uniform the ratio of the Hρ's is the ratio of the ρ's. We could not photograph the first two lines on the same plate as the third, but there are intermediate lines which admit of a comparison in two stages. We were able in this way to verify completely the relative values. For instance, the ratio of the first line to the third from the table is 2·133, whereas the mean of several values on the relative values gave 2·132. This is very strong evidence that the field is really uniform, since any lack of uniformity would give a cumulative error in the two-stage transference.

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* A 1 per cent. change in e/m produces a $\sqrt{1-\beta^2}$ per cent. change in the energy when β is the velocity of the electron.

† Rutherford and Robinson, *loc. cit.*

‡ Danysz, 'Le Radium' (9), 1912, p. 1, and (10) 1913, p. 4.

All measurements of the β-ray groups of thorium B and D that have been given by one of us* are in terms of the old values. In a paper shortly to appear we intend to re-calculate the previous values and to discuss the significance of the change.

Part of the cost of the apparatus used in this work was defrayed by a grant from the Royal Society.

We would like to express our gratitude to Professor Sir Ernest Rutherford for his constant help and advice and to Mr. G. R. Crowe for the preparation of the active sources used.

Summary.

The wave-lengths of the characteristic γ-rays emitted by radio-active bodies can be deduced from the magnetic β-ray spectrum, and it is therefore important to have accurate values of the energies of the groups. It is easy to compare the energies of different groups, and it is sufficient to measure in absolute units the energies of certain of the stronger groups. Those chosen were the prominent ones of radium B.

The quantity Hρ was measured for these groups with an accuracy of 1 in 500, ρ being determined by the usual focussing method and H by a modified balance method in terms of the area-turns of a search coil and the value of a mutual induction. The field used in each experiment was separately determined.

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* Ellis, 'Proc. Roy. Soc.,' A, vol. 101, p. 1 (1922); 'Proc. Camb. Phil. Soc.,' vol. 21, Pt. II, p. 121 (1922).

The Dynamics of Cyclones and Anticyclones regarded as Atmospheric Vortices.

By D. BRUNT, M.A., B.Sc.

(Communicated by Sir Napier Shaw, F.R.S.—Received April 23, 1923.)

In a recent paper* Bjerknes hints that while an anticyclone is a clockwise circulation relative to the earth, it may be regarded as a weak cyclonic or counter-clockwise circulation in space; but he gives no proof of the correctness of this view.

The present paper gives a proof of this view of anticyclones, and discusses a number of points which naturally arise in the course of this proof.

1. *The Gradient-wind Equation and its Solution.*

In the first place it is proposed to consider the motion of air under balanced forces, neglecting the effect of friction. Any element of air then moves along the isobar with the gradient wind velocity. The forces acting on an element of air are

(1) The pressure gradient; and

(2) The so-called "deviating force" due to the earth's rotation.

These produce the centripetal acceleration appropriate to the path. So that, if v be the clockwise velocity and r the radius of curvature of the path in the horizontal plane,† the condition for balanced forces in an anticyclone may be expressed by the equation

$$\frac{v^2}{r} = 2\omega \sin\phi \,.\, v - \frac{\text{pressure gradient}}{\rho} \qquad (1)$$

where ρ is the density of air, ϕ the latitude, and ω the angular velocity of the earth.

It is convenient to write

$$\frac{\text{pressure gradient}}{\rho} = 2\omega \sin\phi \,.\, \mathrm{G}.$$

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* "The Dynamics of the Circular Vortex, &c.," 'Geofysiske Publikationer,' vol. 2, No. 4, p. 59.

† If R be the radius of the earth, and c the angular radius of curvature of the path, $r = \mathrm{R} \tan c$.

Then equation (1) may be written

$$\frac{v^2}{r} - 2\omega \sin \phi \,.\, v + 2\omega \sin \phi \,.\, \mathrm{G} = 0. \tag{2}$$

Solving equation (2) as a quadratic, we find

$$v = r\omega \sin \phi \left\{ 1 \mp \sqrt{1 - \frac{2\mathrm{G}}{r\omega \sin \phi}} \right\}. \tag{3}$$

In order to determine which sign should be taken before the radical in (3), we note that in the case of straight isobars the horizontal centripetal acceleration vanishes, so that the term v^2/r drops out of equation (2), giving $v = \mathrm{G}$; *i.e.*, G is the geostrophic wind. Now equation (3) with upper sign becomes indeterminate when we put $r = \propto$ (or $c = \frac{1}{2}\pi$), but it is possible to expand the quantity under the square root sign and determine its value when r is very large.

$$v = r\omega \sin \phi \left\{ 1 \mp \left(1 - \frac{\mathrm{G}}{r\omega \sin \phi} - \frac{1}{2} \frac{2\mathrm{G}}{r^2\omega^2 \sin^2 \phi} + \text{etc.} \right) \right\}.$$

The upper sign gives

$$v = r\omega \sin \phi \left\{ \frac{\mathrm{G}}{r\omega \sin \phi} + \frac{1}{2} \frac{\mathrm{G}^2}{r^2\omega^2 \sin^2 \phi} + \text{etc.} \right\},$$

or

$$v = \mathrm{G} + \frac{1}{2} \frac{\mathrm{G}^2}{r\omega \sin \phi} + \text{etc.} \tag{4}$$

The solution is therefore continuous near straight isobars.

The lower sign gives

$$v = 2r\omega \sin \phi - \mathrm{G} - \frac{1}{2} \frac{\mathrm{G}^2}{r\omega \sin \phi} + \text{etc.} \tag{5}$$

For indefinitely small curvature of the isobars equation (5) leads to indefinitely large velocities, and therefore this solution of the gradient wind equation demands an infinite discontinuity near straight isobars, since the wind in straight isobars is finite, and equal to G. Such an arrangement would require an infinite supply of energy to set it going, and this is not available in the earth's atmosphere.

Thus the only solution which can be continuous from the centre of a high-pressure region out to straight isobars is that corresponding to the negative sign before the radical. Any system corresponding to the second solution of equation (2) cannot extend out to a region where straight isobars occur. There remains, however, the possibility of the second solution holding in an inner region, and the first solution holding at all points outside this region.

The problem may be treated as two-dimensional. The boundary must of necessity be an isobar since steady motion is along the isobar.

In the first place it should be noted that what we have called the first solution of equation (1) gives $v < r\omega \sin\phi$, as is shown by equation (3), while the second solution gives $v > r\omega \sin\phi$.

In fig. 1 let the radius of curvature at any point P of the boundary be r, C being the centre of curvature of the isobar at P. The plane of the horizon rotates about the vertical with an angular velocity $\omega \sin\phi$ in a counter-clockwise direction, so that the velocity of a point on the earth's surface at P relative to C is $r\omega \sin\phi$. If then v be the clockwise velocity relative to the earth of the air at P, just inside the boundary, its velocity in space is $v - r\omega \sin\phi$ measured clockwise. Outside the boundary the velocity relative to the earth is $2r\omega \sin\phi - v$, since from equations (1) or (3) the sum of the two solutions is $2r\omega \sin\phi$. Hence the velocity in space of the air outside the boundary at P is $v - r\omega \sin\phi$ counter-clockwise. Thus the system contemplated in fig. 1 is that of a closed boundary inside which the circulation is clockwise in space, and outside which the circulation is counter-clockwise in space. No such system has ever been observed in the atmosphere, and, further, since the rotation of the earth is from west to east, the rotation of the earth's atmosphere as a whole is counter-clockwise, and so there appears to be no mechanism in the earth's atmosphere capable of producing a system having a clockwise rotation in space.

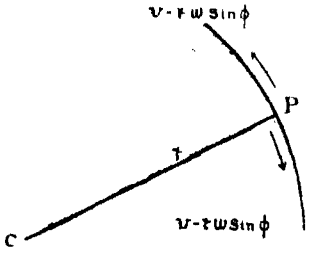

Fig. 1.

But even if such a system could come into existence, it would appear to be unstable. For, since air has a finite coefficient of viscosity, there will be friction at the boundary. The slightest disturbance will lead to mixing of the air from the two sides, and the ensuing mixture will have too large a velocity relative to the earth to balance the pressure gradient, so that it will move inward against the action of the pressure gradient. Once started in this way the whole boundary must break down in a very short time, and the system which holds in the outer region will eventually predominate, though with a readjustment of the pressure distribution.

This argument would appear to break down in one special case, that in which the relative velocity at the boundary is zero, with $v = r\omega \sin\phi$. Physically this means that the clockwise wind distribution in space in the inner region, and the counter-clockwise wind distribution in space in the outer region, both fall off to zero at the boundary, so that there is no discontinuity. But the friction at the ground, and the turbulence which is always associated with motion of the lower layer of the atmosphere, would break down the fine adjustment of the velocity to the value $v = r\omega \sin\phi$, so that the system could not be permanent.

[We may therefore conclude that the second solution of equation (2) may be rejected on the score of instability, leaving as the appropriate value of the gradient wind

$$v = r\omega \sin\phi \left\{ 1 - \sqrt{1 - \frac{2G}{r\omega \sin\phi}} \right\} \tag{6}$$

for anticyclonic motion.

It should be noted that we may pass from anticyclonic to cyclonic motion by changing the direction of curvature of the isobars, which is algebraically equivalent to changing the sign of r in equation (2). The solution for a cyclone is obtained by changing the sign of r in (6), which results in

$$v = r\omega \sin\phi \left\{ \sqrt{1 + \frac{2G}{r\omega \sin\phi}} - 1 \right\}. \tag{7}$$

This solution is continuous with that given in (6) for the anti-cyclone, and gives a distribution of winds blowing counter-clockwise around a centre of low pressure. It may be noted that the rejected solution of equation (2) leads to a clockwise rotation in space for both cyclone and anticyclone, and such a system could not derive its vorticity from the vorticity of the solid rotation of the atmosphere about the earth's axis. The rejected solution for a cyclonic pressure distribution leads to a clockwise wind system relative to the earth.—*Rewritten Nov.* 16*th*, 1923.]

2. *Vorticity in the Anticyclone.*

If the angular velocity of a small element of air in an anticyclone be ζ about the centre of curvature of its path, then 2ζ is called the *vorticity* of the horizontal motion of the element. The velocity of the element of air relative to the earth's surface is then $r\zeta$. It follows from equation (6) that

$$\zeta = \omega \sin\phi \left\{ 1 - \sqrt{1 - \frac{2G}{r\omega \sin\phi}} \right\}. \tag{8}$$

The quantity under the radical must be positive, and from this fact Gold deduced that there is an upper limit to the pressure gradient in an anticyclone. The quantity inside the brackets in equation (8) is always positive, and less than, or at most equal to, unity. Hence ζ can never be greater than $\omega \sin \phi$. In general ζ will be less than $\omega \sin \phi$.

Now in fig. 2, P is a point on the earth's surface. The rotation of the earth may be replaced by a rotation $\omega \sin \phi$ about the vertical at P, and a rotation $\omega \cos \phi$ about the north-south line in the plane of the horizon at P. The plane of the horizon is therefore rotating counter-clockwise in space about the vertical with angular velocity $\omega \sin \phi$. Any element of the anticyclone is rotating clockwise* in this plane at a rate ζ, which is less than or equal to $\omega \sin \phi$. In general, therefore, the plane carries the anticyclone round with it counter-clockwise faster than the anticyclone rotates clockwise in the plane. We conclude, then, that the circulation in space round an anticyclone is in the same sense as that round a cyclone (counter-clockwise). So that if the man on the moon observed the motion of the clouds in an anticyclone through a telescope whose field of view did not take in any portion of the earth's surface, he would conclude that he saw a weak counter-clockwise circulation being carried round bodily by the rotation of the earth.

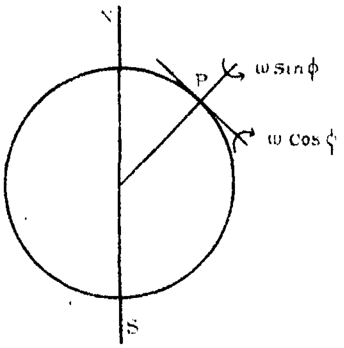

Fig. 2.

The maximum anticyclone revolving as a solid with angular velocity $\omega \sin \phi$ relative to the earth has a velocity distribution

$$\left.\begin{aligned} v &= r\omega \sin \phi \\ G &= \tfrac{1}{2} r\omega \sin \phi \end{aligned}\right\} \qquad (9)$$

i.e., the gradient wind is then twice the geostrophic wind. This is a special case of the principle that in an anticyclone the gradient wind is always greater than the geostrophic wind. This result is readily seen by re-writing equation (2) in the form

$$v = G + \frac{1}{2\omega \sin \phi} \frac{v^2}{r} \qquad (10)$$

and since r is negative in a cyclone, it follows that the gradient wind is less than the geostrophic wind in a cyclone.

The maximum vorticity $2\omega \sin \phi$ becomes zero at the equator, and no anticyclonic circulation can exist as a steady state at the equator. On a non-rotating earth no anticyclonic circulation could exist as a steady state. And from § 3 it would appear that cyclones could not occur on a non-rotating earth.

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* Here and elsewhere in this paper the sense of rotation is in each case that appropriate to the Northern Hemisphere.

3. *Cyclones and Anticyclones regarded as Local Modifications of the Circumpolar Rotation.*

The earth's atmosphere as a whole may be regarded as a large cyclonic whirl, revolving as a solid about the axis of the earth. The large scale circulations in the earth's atmosphere, such as trade winds or monsoons, produce velocities which are small by comparison with the velocities of solid rotation in space about the earth's axis. Any small portion of the earth's atmosphere rotating as a solid about the earth's axis may be regarded as a counter-clockwise whirl, whose vorticity is $2\omega \sin \phi$. For example, if we consider the portion which is above a small circle drawn on the surface of the earth in latitude ϕ, its motion in its own plane is specified completely by a translation of the centre and an angular velocity $\omega \sin \phi$ about the centre. Any small element of the atmosphere may thus be regarded as having a vorticity $2\omega \sin \phi$. The vorticity in space of a cyclone is greater than, that of an anticyclone less than, $2\omega \sin \phi$. Cyclones and anticyclones may therefore be regarded as regions of local enhancement or diminution of the vorticity of the circumpolar whirl. An enhancing of the vorticity is perhaps most easily conceived as the result of removing a portion of the air upwards, so that its place is taken by air converging inward from all sides. By this means samples of air which originally had considerable differences of velocity are brought into close juxtaposition, leading to an increase of angular velocity locally above the normal value $\omega \sin \phi$. In the case where air is removed upwards from a circular area, and is replaced by convergence inward from all sides, the incoming air maintains a constant angular momentum about the centre of the area, and therefore its angular velocity about the centre increases as it approaches the centre. The increase of the vorticity above the normal value $2\omega \sin \phi$ is the characteristic feature of the circulation in a cyclone, and it must always occur when air converges from all sides towards a point. Allowance might be made for the general easterly drift of air in mid-latitudes by using here a value of ω slightly greater than the angular velocity of the earth, but the correction is a very small one.

The characteristic feature of an anticyclonic circulation, *i.e.*, the diminution of the vorticity of the circumpolar whirl below the normal value $2\omega \sin \phi$, may be produced by causing a mass of air to descend and spread outward over the surface of the earth, where it partly displaces, and partly mixes with, the air already in that region. The original angular velocity of the mass of air considered would be $\omega \sin \phi$ about a vertical axis through its centre of mass, but as the angular momentum would be unchanged by the spreading over a greater area, the angular velocity in space must diminish, though it cannot change sign and become clockwise. The result is, therefore, to produce the characteristic feature of an anticyclonic circulation, a diminution of the vorticity below its normal value. But it is only when a very large compact mass of air is caused to descend and completely displace the air over a wide area that the vorticity of the horizontal motion in space over that area can approach zero, yielding the maximum anticyclone with clockwise angular velocity $\omega \sin \phi$ relative to the earth.*

One point which appears to stand out from the preceding discussion is that the process of subtraction or addition of air produces automatically the cyclonic or anticyclonic circulation necessary to balance the pressure gradient.

The vorticity in space of an anticyclone is greatest near the ground, while in a cyclone it is greater above than at the ground. The anticyclone would appear to be dragged round by the ground.

4. *Pressure Distribution in a Revolving Disc.*

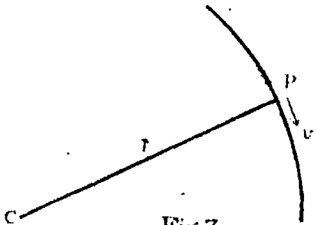

Fig. 3.

Let P be a point on an isobar in an anticyclonic circulation, and let the velocity relative to the earth be v. Let C be the centre of curvature of the isobar at P. $PC = r$. Then if the angular velocity about the point C of the air at P be ζ, $v = r\zeta$. The velocity in space of any element of air at P is $r(\omega \sin \phi - \zeta)$, while the velocity in space of the observer, relative to C, is $r\omega \sin \phi$. Now the condition from which we derive the equation of motion may be stated thus :—

"The gradient of pressure balances the acceleration of the air relative to the observer who measures the pressure."

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* The effects of convergence to, and divergence from, an axis, consequent upon removal or addition of air along that axis, were discussed by the present writer in a paper, entitled "The Dynamics of Revolving Fluid on a Rotating Earth," 'Proceedings, Royal Society,' A, vol. 99, p. 397 ; with results very similar to those here derived.

In fig. 3 the acceleration of air at P relative to an observer on the earth at P

= acceleration of air at P relative to C — acceleration of observer at P relative to C.

Therefore
$$\frac{1}{\rho}\frac{\partial p}{\partial r} = r(\omega\sin\phi - \zeta)^2 - r\omega^2\sin^2\phi \tag{11}$$

or
$$\frac{1}{\rho}\frac{\partial p}{\partial r} = -r\zeta(2\omega\sin\phi - \zeta) \tag{12}$$

If we again substitute $\zeta = v/r$, this equation reduces to equation (1), from which we started, and so equation (12) may be used to show the magnitude and direction of the "deviating force" due to the earth's rotation.

For a disc revolving as a solid, ζ is constant for all values of r. If we neglect variations of ρ and ϕ the integration of equation (12) gives

$$\frac{p - p_0}{\frac{1}{2}\rho} = -\zeta(2\omega\sin\phi - \zeta)r^2. \tag{13}$$

This gives a system in which pressure decreases outward from the centre for all positive values of ζ. The corresponding equation for a cyclone revolving as a disc with angular velocity ζ' in a counter-clockwise direction is obtained by substituting $-\zeta'$ for ζ in equation (12).

$$\frac{1}{\rho}\frac{\partial p}{\partial r} = r\zeta'(2\omega\sin\phi + \zeta') \tag{14}$$

giving on integration, assuming ρ and ϕ constant,

$$\frac{p - p_0}{\frac{1}{2}\rho} = \zeta'(2\omega\sin\phi + \zeta')r^2. \tag{15}$$

Equation (15) was given by Sir Napier Shaw in 'Geophysical Memoir' No. 12.

Equation (13) can be applied to give a rough estimate of the angular velocity in an anticyclone. For example, the Daily Weather Report of November 16th, 1922, showed an anticyclone centred over Wales. The pressure at the centre was about 1,041 mb. while the pressure at 1,000 km. from the centre (Thorshavn) was 1,028 mb. Assuming $\rho = 0{\cdot}0013$ gm./cm.^{3}, $\phi = 55°$, $r = 10^8$ cm., and $\omega\sin\phi = 6\,.\,10^{-5}$, we find

$$(\omega\sin\phi)^2 - (\omega\sin\phi - \zeta)^2 = 2\,.\,10^{-9},$$

or
$$\omega\sin\phi - \zeta = 4\,.\,10^{-5}$$

and
$$\zeta = 2\,.\,10^{-5} = \tfrac{1}{3}\omega\sin\phi.$$

It is not suggested that the anticyclone referred to was of the nature of a disc revolving like a solid, but the above computation gives an estimate of the mean value of the vorticity over the range considered.

A similar computation for the cyclone of December 16th, 1917, gave a mean counter-clockwise angular velocity of $1 \cdot 6\ \omega \sin \phi$ relative to the earth. This is probably a higher value than the average for cyclones which pass over the British Isles.

5. *The Pressure Distribution in the Circumpolar Whirl.*

It is not difficult to convince oneself that a uniform distribution of pressure over the whole surface of the earth characterises the circumpolar whirl.* For at any point P in latitude ϕ the acceleration towards the centre M of the small circle in which P revolves is $R \cos\phi \,.\, \omega^2$, where R is the radius of the earth. The component acceleration directed towards North is $R \cos\phi \sin\phi \,.\, \omega^2$. At first sight it might appear that this acceleration demands a pressure gradient of corresponding magnitude directed towards the pole. But since this is also the acceleration of any particle on the earth's surface it follows, since bodies can and do remain at rest relative to the earth's surface, that there must be a balancing force.

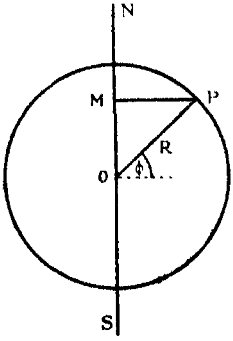

Fig. 4.

This balancing force is to be found in a component of gravitational attraction along the earth's surface. The shape of the earth is such as to give at all points a horizontal component of gravitational attraction exactly equal to $R \cos \phi \sin \phi\ \omega^2$. There is therefore no horizontal pressure gradient in the circumpolar whirl rotating as a solid, and pressure is the same at all points in a horizontal surface (except in so far as insolation, radiation, etc., may cause local variations). Further, it does not matter whether the pressure is measured by an observer fixed on the earth or by one who does not participate in the earth's rotation. In either case the horizontal field of pressure of the circumpolar whirl is uniform over the whole earth.

Since we have seen in fig. 2 that any small portion of the earth's surface may be regarded as rotating with angular velocity $\omega \sin\phi$ about the vertical, we may also say that any small portion of the circumpolar whirl is a small whirl of vorticity $2\omega \sin\phi$. But to regard it as a centre of low pressure for that reason would be contrary to the fact that the field of pressure is uniform. A deviation of the field of pressure from uniformity can only occur when the vorticity deviates from its normal value $2\omega \sin \phi$, and in evaluating the field of pressure corresponding to any particular distribution of vorticity it must always be remembered that the standard state for uniform pressure is not vorticity zero, but vorticity $2\omega \sin \phi$.

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* The name is here applied to the whole atmosphere rotating as a solid about the earth's axis.

It is important to remember this when we come to attempt to evaluate the pressure distribution in an anticyclone, as it would be evaluated by an observer who did not participate in the rotation of the earth. One is tempted to say that in equation (11) previously derived,

$$\frac{1}{\rho}\frac{\partial p}{\partial r} = r(\omega \sin \phi - \zeta)^2 - r(\omega \sin \phi)^2 \qquad (11)$$

the second term on the right-hand side, being the acceleration of the terrestrial observer, should now be omitted when the pressure is measured by an observer who does not participate in the earth's rotation. But dropping out the second term changes the sign of the right-hand side, so that apparently the anticyclone would appear to be a low-pressure centre to an observer fixed in space.

It is, however, a simple matter to show that the argument used in the last paragraph is fallacious. For it assumes that the absence of vorticity corresponds to a uniform pressure distribution, an assumption which has been shown above to be false. If we wish to look upon an anticyclone from the point of view of an observer fixed in space, we must proceed as follows :—

The anticyclone has clockwise angular velocity ζ relative to the earth, or counter-clockwise angular velocity $\omega \sin \phi - \zeta$ in space. The acceleration of P relative to C (fig. 3) is $r(\omega \sin \phi - \zeta)^2$ in the actual case considered, and would have been $r(\omega \sin \phi)^2$ in the case where P was regarded as a part of the circumpolar whirl. The deviation of the pressure distribution from uniformity must balance the difference between these two accelerations ; or,

$$\frac{1}{\rho}\frac{\partial p}{\partial r} = r(\omega \sin \phi - \zeta)^2 - r(\omega \sin \phi)^2$$

which is the same as equation (11) previously derived. Hence to an observer of the motion of the air in space the anticyclone remains a centre of high pressure.

6. *Summary.*

In the first place, the gradient wind equation is written down and solved algebraically as a quadratic. Reasons based on considerations of continuity, energy supply, and stability are adduced for rejecting one solution. The form of the solution of the equation for an anticyclone shows that there is an upper limit to the angular velocity of any portion of an anticyclone about the instantaneous centre of curvature of its path. This upper limit is $\omega \sin \phi$, so that the anticyclone viewed from outside the earth is being carried round counter-clockwise by the rotation of the plane of the horizon faster than it rotates in that plane. Hence an observer outside the earth would see an anticyclone as a counter-clockwise circulation in space. The question naturally arises, would he also regard it as a centre of low pressure? It is found on examination that an anticyclone will always appear to be a centre of high pressure.

The rotation of the earth's atmosphere as a solid about the axis of the earth forms a circumpolar whirl, in which the field of pressure is everywhere uniform. It is shown that a cyclone and an anticyclone may be regarded as a local enhancing or diminution of the vorticity of the circumpolar whirl.

On the Degradation of Acoustical Energy.

By Morris D. Hart, A.M.I.E.E., D.I.C., M.Sc., A.Inst.P.

(Communicated by Prof. A. N. Whitehead, F.R.S.—Received November 20, 1923.)

Introduction.

This paper forms part of an investigation the object of which was to study the best means of producing sound signals for use over long ranges, with special reference to the improvement of existing forms of sound-signalling apparatus.

The over-all efficiency of the appliances at present in use is notoriously low; King,[*] working with a diaphone, concluded that of 35 h.p. supplied as compressed air only 2·4 h.p. were actually converted into sound, and estimated that of this only 0·3 h.p. remained at a range of 10 nautical miles. Similar low efficiencies have been noted by other workers, and in particular it has been observed that an increase in the power absorbed by the source (*e.g.*, in the pressure of the air supply in the case of a siren) is not attended by anything approaching a proportionate increase in the range of the sound produced.

[*] 'Phil. Trans.,' A, vol. 218, pp. 211–293.

It is clear, therefore, that there is great scope for both theoretical and experimental study in this field, where designers have in the past been severely handicapped by the absence of established principles of technique. Certain of these principles such as the choice of frequency and the value of directive sources will necessarily vary in different cases, but others, notably the behaviour of sound waves passing through a medium, are invariably applicable.

In the operation of any source of sound two processes may be distinguished :

(*a*) The conversion of mechanical, electrical or some other form of energy into sound.

(*b*) The transmission of this sound through the medium surrounding the source.

For the sake of convenience we will refer to these as process (A → B) and process (B → C) respectively, where A represents the stage at which the energy is present in some form other than sound, B that a B)hich it is in the form of sound at the source, and C that at which the sound has been transmitted some distance through the medium.

The process (A → B) is entirely dependent on the nature of the sound-producing apparatus, whereas the process (B → C) depends only on the acoustical energy present at stage B and on factors independent of the type of source used, such as the nature and extent of the medium. This paper will be confined to the discussion of the process (B → C) the treatment of which is equally applicable to every type of source.

In practice the transmission of sound from one point to another is affected by two sets of factors which may be described as acoustical and meteorological respectively. The former comprises only the physical properties of air and the intrinsic qualities of sound ; the latter includes all the complicating causes, such as wind and temperature gradients, atmospheric turbulence, and the like, which may raise or depress the " acoustical horizon " and cause the propagation to differ from what would happen in their absence. For the present purpose only the acoustical factors are of interest and we shall therefore always assume that the propagation of process (B → C) takes place through a homogeneous and isotropic medium.

In all cases of practical importance we are necessarily concerned with waves of finite amplitude ; it has therefore seemed better to approach the subject as far as possible *de novo* rather than to attempt the development of a mathematical treatment from the classical equations of acoustical theory ; for these involve assumptions which approximate to the truth only for very small amplitudes. It is believed that the concept of the degradation of acoustical energy as developed below should lead to conclusions of immediate practical application, even although it may not yet be possible to give a complete parallel treatment in terms of first principles.

ACOUSTICAL DEGRADATION.

A. *Theoretical Considerations.*

In considering the propagation of sound waves through still homogeneous air it is customary to assume the validity of the Law of Inverse Squares for the acoustical energy flux.* Provided that no acoustical energy is either absorbed or supplied by the medium, this assumption is evidently justified, but there are good reasons for supposing that loss of acoustical energy does take place in the medium in the case of sounds of finite amplitude.

Sound waves are normally propagated under almost perfectly adiabatic conditions, and Stokes showed that any appreciable divergence from the adiabatic cycle would necessarily lead to a rapid stifling of the sound.† For small amplitudes the divergence is negligible at all ordinary frequencies but it seems likely that when very large amplitudes and pressures are involved the variation of temperature during the cycle may be great enough to admit of a significant transference of heat even during the very short time available. This would lead to a more rapid decrease of energy flux with distance than is indicated by the inverse-square law and would be especially effective in the case of low frequency sounds in which the time available for radiation is greatest.‡ It may be noted that the heat thus dissipated by radiation must necessarily be transferred from the regions of high pressure to those of low pressure (*i.e.*, from the "crests" to the "troughs") thus tending to reduce the difference of pressure between them.

In addition to this, it is easy to show that the velocity of propagation of the "crests" of a train of sound waves must be greater than that of the "troughs" so that the former constantly tend to overtake the latter.§ On the assumption that the waves are plane, that the law of pressure for the gas remains unchanged and that the influence of viscosity is negligible this process must sooner or later result in a state of motion which is physically impossible so that some kind of "discontinuity" would set in. But in practice we are always concerned with spherical waves "whose divergency may of itself be sufficient to hold in check the tendency to discontinuity."* Moreover, "in actual gases it is certain that before discontinuity could enter, the law of pressure would begin to change its form, and the influence of viscosity could no longer be neglected."* We need not therefore fear any actual discontinuity although the wave-form must necessarily be distorted to some extent. Whether this distortion will be limited to the production of harmonics at the expense of the original sound or whether, in addition, vortices may also be produced is not yet clear, but it seems certain that any pure sound will steadily lose a proportion of its energy on account of this distortion.

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* It is important to notice that even in the ideal case when this law holds exactly so far as acoustical energy flux is concerned, it does not follow that the other physical correlates of the sound—*e.g.*, condensation, velocity or pressure are linear (or second order) inverse functions of the distance from the source. It can in fact be shown that this is not always the case, even for small amplitudes, when the distances concerned are not large compared with the wavelength.

† Rayleigh, 'Theory of Sound,' vol. II, p. 24 (1896).

‡ *Ibid.*, p. 23.

§ *Ibid.*, p. 33–37.

It is of course true that the creation of these harmonics does not alter the total acoustical energy flux, but for practical purposes it is desirable to confine the discussion to the fundamental frequency of the sound concerned, since it seems very unlikely that this process of distortion could ever lead to the generation of harmonics audible at a greater distance than the fundamental unless the latter were itself of sub-audible frequency.

Throughout this paper, accordingly, the word "intensity" will be used to denote the amount of energy flux per unit area due to the fundamental of the sound concerned and not the total flux due to the fundamental and all the harmonics. It follows from the foregoing that the process of propagation (B$\rightarrow$C) may take place less favourably than is indicated by the inverse-square law, if at stage B (or, indeed, at any other stage between B and C) the conditions be such as to bring either of the above-mentioned factors (or others such as viscosity) saliently into play.

If E_a and E_b be the intensities (ergs per sq. cm. per second) of a sound at two points distant "a" and "b" respectively from any source (b being assumed greater than a), then if the inverse-square law hold good, $E_a a^2$ and $E_b b^2$ will be equal, and we may speak of the *actual* ratio $E_b b^2/E_a a^2$ as the Transmission Efficiency (${}_a\eta_b$) between the two points. This efficiency will approximate to 100 per cent. when E_a is very small, but so soon as the latter becomes large enough to make the thermal losses or the distortion losses important the efficiency will be reduced and the curve connecting transmission efficiency and intensity will clearly be of the general form shown in fig. 1.

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* Rayleigh, *loc. cit.*, p. 36.

We may now define the "Degradation Coefficient" of a sound of any intensity "E" at any frequency "n" in terms of the rate of loss of energy from the fundamental of that sound, and the loss per period from unit volume of the medium at any point may be written ${}_n\Omega_E$ of the acoustical energy due to the fundamental of that sound transmitted across unit area per second at that point.

The connection between the degradation coefficient and the transmission efficiency may be shown to be :—

$$a^2E_a(1 - {}_a\eta_b) = n\int_a^b r^2\,{}_n\Omega_r\,.\,E_r\,.\,dr.$$

By methods to be described later it is possible to determine the values of ${}_n\Omega_E$ for any frequencies or intensities from measured values of E.

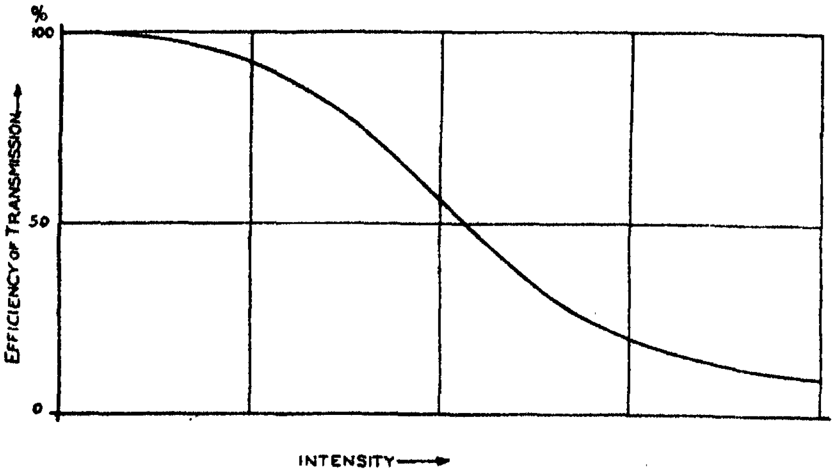

Fig. 1.

Conversely, if the relations between n, E and ${}_n\Omega_E$ be known, the transmission efficiency of a sound of any given frequency and intensity, and for any values of "a" and "b" may be determined.

It seems probable on general grounds that the rate of increase of ${}_n\Omega_E$ with respect to E may increase with E so that the rate of loss of energy from the medium between two concentric spherical surfaces $\left(i.e.,\ 4\pi n\int_a^b {}_n\Omega_r\,.\,E_r\,.\,r^2\,.\,dr\right)$ will become increasingly serious as moderate values of E are exceeded, and as the radius of the lesser sphere is reduced. Thus sources of small intensity and large area are likely to be more efficient than sources of great intensity and small area producing the same intensity of sound at a given distance.

So far as the process (B → C) is concerned, it seems probable that a complete series of values of ${}_{n}\Omega_{E}$ is all that is required for the solution of all concrete problems in sound transmission, for if once they be determined they will enable us to predict the behaviour of any sound in any particular case without the necessity of deducing the relevant laws from first principles—a problem which has hitherto proved insoluble by the ordinary process of mathematical analysis.

The foregoing depends on the assumption that only a single relation of the form ${}_{n}\Omega_{E} = f\,(n,\ E)$ exists. That this condition is likely to be satisfied to a degree of approximation sufficient for all practical purposes may be shown as follows :—

Consider an elemental portion of a "tube of force" (*i.e.*, a volume bounded as to its ends by portions of successive wave fronts and as to its sides by surfaces everywhere normal thereto), and let the dimensions of this volume be large compared with the amplitude of the sound, but indefinitely small compared with the radius of curvature of the wave front at any point within the volume. (The case in which the radius of curvature and the amplitude are comparable will never occur in practice and may be definitely excluded; in all other cases such a volume may be postulated.) Since all the dimensions of this volume are small compared with the radius of curvature, it follows that, to the same order of approximation, the two areas forming its ends will be equal; and since, by definition, its sides are formed of surfaces normal to equipotential surfaces, there can be no transference of acoustical energy across them.

Let the energy flux across one end of the volume and the frequency of the sound be specified. Then, assuming that the distribution of energy flux over the portion of wave front forming the end of the volume is uniform, and since the space rate of change of the mean molecular density along the volume is negligible to the order of approximation used, the motion must be completely determined (to the same order of approximation) by the properties of the medium which alone can influence the relations which subsist between the various correlates constituting the total state of motion.

It follows that since the rate of loss of acoustical energy taking place in this volume is indissolubly connected with the state of motion and nature of the medium therein the Degradation Coefficient which is defined by this loss must be an invariable function of the energy flux to the order of approximation used.

This argument assumes that the rate of loss of energy from the fundamental of the sound is unaffected by any harmonics which may be present. This is not necessarily true on *a priori* grounds, for it is possible that the rate of loss of energy by distortion from the fundamental of a sound may depend not only on the intensity of that fundamental but also on the shape of the wave at the point considered, *i.e.*, on the intensities and phases of the harmonics present. The theory of wave motions of finite amplitude is not yet sufficiently developed to make it clear whether the constituents of a complex sound can be treated as independent entities, to the extent of assuming that the rate at which the energy in each is converted into the form of higher harmonics is unaffected by the presence of the others. If this measure of independence be not realised the value of ${}_n\Omega_E$ for the same values of n and E will vary in different cases with the distance from the source at which the intensity of the sound is E; for even if the sound wave were purely sinusoidal at the source the amount of harmonics generated, which depends on the distance over which the process of distortion is operative, will vary in the different cases. It seems legitimate, however, to make this assumption in dealing with all practical problems. In the first place the influence of the wave form on the rate of loss of energy due to distortion is a second order effect, even if it exist at all, and secondly the higher harmonics generated are liable to rapid dissipation by atmospheric turbulence etc., so that in practice the effect is not likely to be cumulative.

B. *Experimental Work.*

1. *Theory of the Determination of* ${}_n\Omega_E$.—As already stated above, it is possible to determine the values of ${}_n\Omega_E$, for any frequencies or intensities, from measured values of E. This may be done as follows :—

Suppose that the values of E_r have been determined, for a constant intensity of source, at a number of points between $r = a$ and $r = b$. Then, we may write :—

$$-d\,(r^2 E_r) = nr^2 \,.\, {}_n\Omega_r \,.\, E_r \,.\, dr, \tag{i}$$

or

$$-\frac{d}{dr}\,(\log_e r^2\, E_r) = n\, {}_n\Omega_r. \tag{ii}$$

Whence the values of ${}_n\Omega_r$ may be determined for any value of r and hence for the corresponding value of E. By varying the strength of the source a complete curve may be obtained for any frequency.

It will be seen that in order to obtain values of ${}_n\Omega_E$ it is necessary to measure the acoustical energy flux. So far as the present writer is aware, however, no means exist for doing this directly; it can only be deduced from measured values of some other quantity such as the pressure, on the assumption that the relation which is known to connect these correlates at indefinitely small amplitudes is valid.

Nothing appears to be known as to the intensities at which the deviations from such relations become significant, but if these should be less than or equal to those at which the values of ${}_{n}\Omega_{E}$ become appreciable, it is clear that the experimental determination of the latter is impossible until the relations subsisting between the various correlates at these intensities have been discovered. It is, however, at least possible that significant values of ${}_{n}\Omega_{E}$ may exist in regions of intensity where the values of the energy flux as calculated in the ordinary way would be very approximately correct.[*]

In any event a quantitative study of the conditions prevailing in the immediate neighbourhood of a source of moderate power is likely to yield interesting and informative results. It was therefore decided to make such a study using the Resonated Hot-wire Microphone[†] as being the most practical means of obtaining quantitative data. This instrument gives indications which are a measure of the pressure changes outside its neck, and in cases where the ordinary relation between pressure and energy flux holds good, the value of the latter may be calculated.

For small amplitudes and if no loss take place the pressure in the neighbourhood of a source varies inversely as the first power of the distance. If this relation be found by experiment to hold in any particular case, it follows either that the values of the Degradation Coefficient are negligible or that there is exact cancellation of the effects due to the losses by those due to the divergence from the normal pressure-intensity relation.

If, on the other hand, it be found that the pressure-distance relation does not hold, one of two alternatives is indicated. Either the normal pressure-intensity relation is invalid, in which case no quantitative conclusions can be drawn, or else the values of ${}_{n}\Omega_{E}$ can be determined.

The experimental results have actually been treated on the basis of this latter assumption, but it should be noted that this may be incorrect, in which case the experiment is only capable of qualitative interpretation.

2. *The Principle of the Experiment.*—The experiment consisted in obtaining, at a given frequency, sets of corresponding values of quantities representing the strength of the source and the intensity of the sound produced at different

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[*] Compare, for example, the case of Ohm's law, which holds good in spite of the fact that energy is dissipated in the form of heat produced by the passage of the current.

[†] For the theory and calibration of these instruments see Tucker and Paris, 'Phil. Trans. Roy. Soc.,' A, vol. 221, pp. 389–430.

distances from it. This plan was adopted because of the impracticability of ensuring a constant power output from the source while taking a series of observations at the various distances required. For indicating the strength of a source a special "check" microphone was devised which is described below.

3. *The Source of Sound.*—For this purpose a Seebeck type of siren was selected, and was specially designed so as to reduce the wastage of air to a minimum.

In order to obviate sources of error which might otherwise arise from reflection from the ground, a pit was prepared at a distance of 200 ft. from the nearest building and of such a size as to accommodate the siren and motor with the orifice just at the level of the ground. The air supply was provided by a compressor which, however, was incapable of maintaining a head of more than about 4–5 lb. per square inch at the speeds used.

4. *Microphones.*—As already mentioned, it was decided to employ the Hot-wire Microphone. As will appear later this method possesses certain disadvantages both as regards the difficulty of accurate calibration for obtaining absolute values and in the matter of susceptibility to wind, but it was adopted on account of its great convenience and the accessibility of suitable apparatus.

For measuring the intensity of the sound two "standard" microphones were prepared of resonant frequencies 100 and 200 v/sec. respectively.

The "check" microphone consisted of a small brass container fitted with a "neck" and hot-wire grid in the usual way but instead of being exposed to the outer air the neck was connected by a length of rubber tube to a small needle valve inserted into the siren air supply pipe immediately behind the orifice. By this means the necessity of providing a separate "check" microphone for each "standard" was obviated, adjustment to suit different strengths of source was facilitated and all possibility of interaction between standard and check microphones was avoided. Since the microphone so arranged was "aperiodic" for the frequencies used a stroboscopic speed indicating device was arranged so as to ensure the corresponding deflections being read at the same frequency of sound in all cases.

5. *Electrical Arrangements.*—(*a*) For the measurement of the effects produced on the "standard" and "check" microphones the Wheatstone's bridge method was adopted, balance being secured by variation of the grid current. This is superior to the more usual method of altering the balancing arm of the bridge, since it results in the grid being brought to the same resistance and hence to the same temperature whenever balanced. Consequently, if, as was always

the case in practice, the balancing grid current is constant, the deflections observed are an invariable function of the change of grid resistance which causes them.

(*b*) In order to enable the experimenters, who necessarily worked in the immediate vicinity of the siren, to assure themselves that the proper pressure was being maintained by the compressor a special instrument was devised, to which the name of Telemanometer has been given.

This consists of a small brass vessel fitted with a hot-wire grid and holder of the usual pattern at one end, while a small hole is pierced at the other. The neck of the grid holder is connected to the compressed air reservoir by a rubber tube and needle valve in the same way as the check microphone was connected to the air supply pipe of the siren.

The grid is connected in the usual way into a bridge which is balanced with the needle valve closed or with no pressure in the reservoir. The valve is then opened until the flow of air from the reservoir past the grid is sufficient to cause a suitable deflection of the galvanometer. In practice the bridge was located in the laboratory near the compressor and duplicate galvanometers were provided, one near the bridge and the other on the instrument table, so that variations of pressure could be observed at either place as desired. This instrument proved very satisfactory and reliable in use; its readings are perfectly steady and the galvanometer deflections could easily be calibrated against a standard pressure-gauge.

6. *Procedure.*—The experimental procedure was as follows :—

The two microphones were balanced and allowed to remain with the current flowing through the grid until it appeared that a steady condition had been attained. As a precautionary measure observations were taken at the beginning of each set of readings of the voltage, series resistance and balancing current in order to guard against possible errors arising from variations in external conditions.

Sets of observations were then taken with the standard microphone at a fixed distance from the source, but with different openings of the main air valve. The check microphone needle-valve and galvanometer sensitivity were so adjusted as to give a fullscale deflection for that setting of the main air valve which gave the maximum permissible deflection of the standard microphone galvanometer. These adjustments were kept constant for all the sets of observations. Zero readings were, of course, taken at the beginning and end of each series of observations.

In taking these observations one experimenter was responsible for reading *the two galvanometers, the other for controlling the speed of the siren motor, for observing the stroboscopic speed-indicator and for recording the readings.*

For each observation the siren was run up through the "check" and "standard" speeds.* The check galvanometer was read when the check speed was indicated by the second experimenter, and the reading of the standard galvanometer was taken when it reached a maximum.

This procedure was repeated with the standard microphone at each desired distance from the source.

7. *Theory of Treatment of Observations.*—Subject to the reservations made above, the theory of the treatment of the observations thus obtained is as follows :—

If the values of the deflections of the check galvanometer be plotted against those of the standard galvanometer a curve will be obtained corresponding to each distance of the standard microphone from the source. Thus the observations at each standard frequency yield a family of such curves which may be plotted on a single chart with, say, the check deflections as abscissæ. The intercepts of any vertical ordinate with these curves represent for a constant strength of source the deflections of the standard galvanometer corresponding to the various distances from the source for which the curves are respectively drawn.

If the standard microphone has been calibrated, these deflections may be converted into absolute intensities of sound and the values of simultaneous intensities at different distances are thus obtained. From these data the values of $1/n \log_e r^2 E_r$ can be calculated and plotted against the corresponding values of "r." The slope of any one of these curves at any point gives the value of ${}_n\Omega_E$ for the frequency concerned and for the intensity corresponding to the point in question.

8. *Accuracy and Experimental Conditions.*—Very great difficulties of all kinds were encountered in the course of the work. For external reasons it was necessary to take the observations during a month which was characterised by exceptionally unfavourable climatic conditions. Wind and rain constantly made accurate work impossible, and although some hundreds of observations were made under fair or good conditions, a much larger number would have been obtained in the time available if interference by the bad weather could have been eliminated. Unfortunately, the liability to such interference is inseparable from open-air work with apparatus of the type used.

Other serious difficulties arose from the procedure necessary in order to calibrate the hot-wire microphone in such a way as to yield absolute values. This procedure is fully described in the paper on the subject by Dr. W. S. Tucker and Dr. E. T. Paris,* by which the present writers have been guided throughout.

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* The "check speed" was 1/12 below the "standard speed."

For example, the grid calibration curve could not accurately be represented by an equation of the form

$$D = -D_0 + a(u + u_0)^2 + b(u + u_0)^4.$$

It was therefore necessary to adopt a compromise and to select values for "*a*" and "*b*" such that the resulting expression, though not complying perfectly with the conditions imposed by physical considerations yet represented the experimental points with fair accuracy.

A further possibility of error appears to be involved in the assumption that "the resistance of the grid at any instant is the 'equilibrium' value which it would take up if the instantaneous velocity were maintained."† This is clearly only true if the thermal "lag" of the grid is negligible. It is certainly very small, but may become relatively important when compared to the scale of magnitudes of the thermal changes which take place. This appears the more probable in the light of the known insensitivity of the hot-wire microphone to sounds of high frequency.

It should be noted that the sense of any errors arising from this cause will be such as to obscure effects due to degradation of acoustical energy and they are therefore incapable of giving spurious indications of the degradation coefficient in cases where its value is actually negligible. For any "lag" there may be in the response of the grid will be most pronounced when the time rate of change of the velocity of the alternating air current is greatest, so that, at a given frequency, the galvanometer deflections and therefore the apparent intensity will be reduced in a proportionately greater degree for the more intense sounds.

It consequently became apparent that it was not possible to calibrate the microphones to a high order of accuracy unless an exhaustive study were first made both of the precise form of the calibration curve and of the possibilities of error arising from the thermal "lag" of the grid. Since the quality of the actual observations obtained was in some measure vitiated by the climatic conditions already referred to, it was decided that ancillary investigations of this magnitude would be unjustifiable.

The relation having been thus determined between standard galvanometer deflections and U^2, where U sin *pt* represents, in cubic centimetres per second, the instantaneous value of the alternating air flow in the neck of the resonator, it only remains to evaluate the constant whereby the values of U^2 may be converted into absolute intensities of sound outside the resonator. As an example, the case of the 100 v/sec. resonator may be considered. For this the "magnification" $Vc/2k$ given on page 401 of the paper quoted above (which, it should be noted, compares the air flow in cubic centimetres per second inside the neck with the flow in cms. per second outside the neck) was found to have the value 96 sq. cm.

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* 'Phil. Trans.,' A, vol. 221, pp. 389–430.

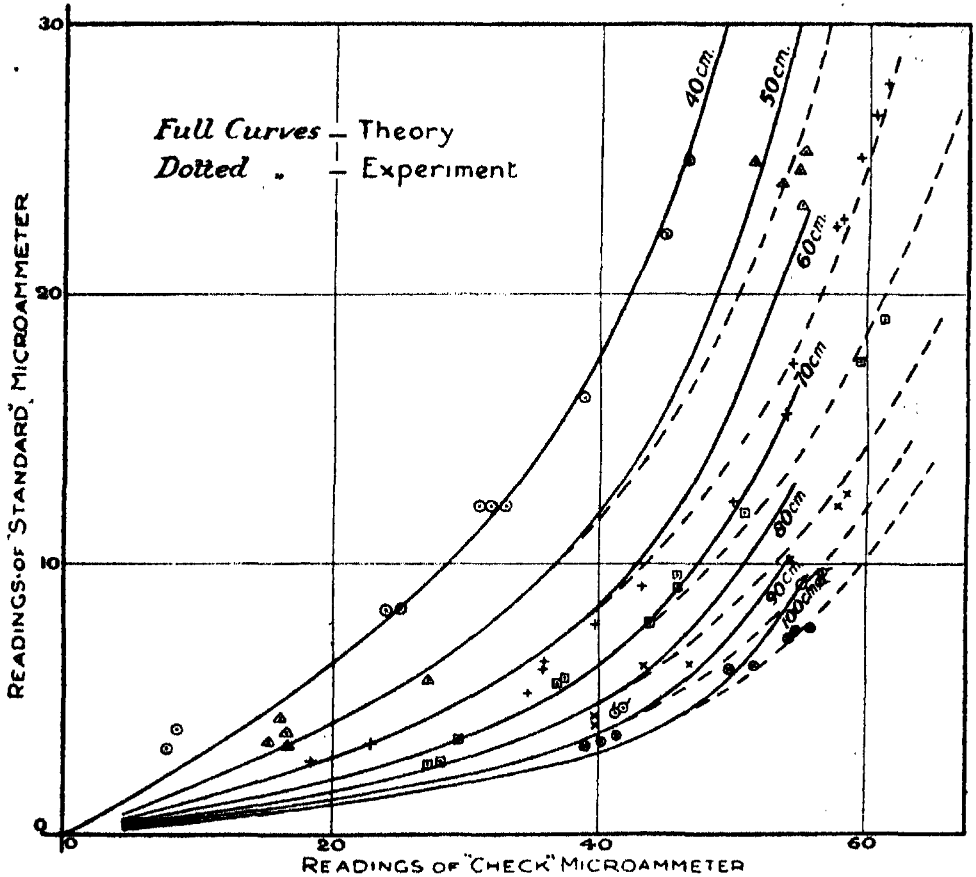
† *Loc. cit.*, p. 409.

The values of "c" the conductivity, and "k" the damping factor, were determined in the usual way and amounted to 0·16 cm. and 28·2 sec.$^{-1}$ respectively. Hence it may be calculated that an air flow of 1 c.c. per second inside the neck corresponds to an intensity of $2{\cdot}24 \times 10^{-3}$ ergs per sq. cm. per second outside the neck. Since, however, the value of the "magnification" given above is only an approximation which becomes decreasingly accurate as the intensity increases, it follows that another source of error is introduced at this point. The sense of the intensity-rate of change of this error is almost certainly the same as that produced by increase of "K" with intensity (compare the phenomenon of "saturation" of resonators), and consequently the effect will be, like that of the thermal lag of the grid, to render the detection of significant degradation coefficients more difficult.

9. *Interpretation of the Observations.*—Fig. 2 shows all the points obtained with the 100 v/sec. resonator. Of the family of curves referred to on page 90 only one, namely, that corresponding to a distance of 40 cms. from the source, can be drawn with certainty. It is, however, possible to obtain immediate evidence of the existence of a significant degradation coefficient by deducing from this curve the forms which the others would take if the wastage of energy were negligible. The absolute intensity corresponding to any point on this "40 cm." curve can be obtained by virtue of the calibration described above, and if the value of the degradation coefficient were negligible it is clear that the intensity at any other distance, "r" cm., for the same strength of source would be obtained by multiplying this intensity by $40^2/r^2$; this value can be converted again into deflection, and thus for any distance a number of points can be calculated and a curve drawn on which the experimental points would lie if the degradation coefficient were negligibly small.

These curves are shown by the full lines in the figure, and it is at once apparent by inspection that at the higher intensities the experimental points have a strong tendency to lie below these curves—*i.e.*, to indicate unduly low intensities—for distances from the source greater than 40 cm., and to group themselves about the curves indicated by the dotted lines.

It should be noted that the experimental points which lie near the origin are less reliable than those corresponding to the higher intensities, because of the proportionately greater effect produced by variations of zero. In this region also the values of $_{n}\Omega_{E}$ are necessarily small, so that the dotted and full curves must closely approximate.



Experimental Points on 40 cm. curve shown .... ⊙
,, ,, 50 ,, ,, ... △
,, ,, 60 ,, ,, ... +
,, ,, 70 ,, ,, ... ⊡
,, ,, 80 ,, ,, ... ×
,, ,, 90 ,, ,, ... σ'
,, ,, 100 ,, ,, ... ⊗

Fig. 2.

The divergence of the two sets of curves is in itself enough to prove that the ordinary pressure-distance relation does not hold at the amplitudes here involved, and although it is clear that the dotted curves cannot be drawn with sufficient precision to enable absolute values to be determined with great accuracy, it is possible to obtain, by the method described above, approximate estimates of the values of $_n\Omega_E$ for this frequency and in this region of intensity.

The actual values obtained are given below :—

Ergs per sq. cm. per sec. × 10^4	$_{100}\Omega_E$.
4	0·27 cm.$^{-1}$.
8	0·78 ,,
12	1·52 ,,
16	2·41 ,,

These values are taken from a fair curve through the experimental points; both are shown in fig. 3.

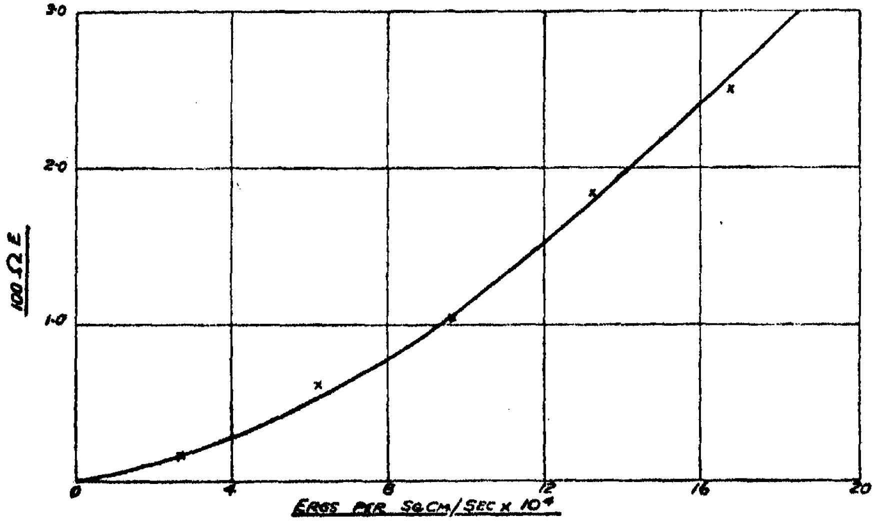


FIG. 3.

Since every value of the strength of the source is capable of yielding a curve the slope of which determines the value of $_n\Omega_E$, and since the values of E for these curves necessarily overlap, it follows that values of $_n\Omega_E$ for a given intensity, which are *ex hypothesi* equal, can in each case be obtained from points on several of these curves. This provides a useful check on the reliability of the figures obtained, and the fact that the curve shown in fig. 3 is based on determinations corresponding to several different strengths of source shows that the final results are satisfactorily consistent *inter se*.

Similar but merely qualitative evidence of the failure of the normal pressure-distance relation was obtained in the case of the note of frequency 200 v/sec.

10. *The Significance of the Results.*—These results show that in the neighbourhood of even so small a siren as that used in these experiments, the working pressure of which never rose above 4 or 5 lbs. per sq. inch, very considerable losses occurred. Thus with approximately this pressure on the siren the intensity at 40 cm. from the source was $2 \cdot 52 \times 10^{-3}$ ergs per sq. cm. per second, and at 100 cm. it was $3 \cdot 43 \times 10^{-4}$. The transmission efficiency was therefore $\frac{3 \cdot 43 \times 100^2}{25 \cdot 2 \times 40^2} = 0 \cdot 845$, so that no less than 15·5 per cent. of the acoustical power at 40 cm. from the source was lost before the sound reached a distance of 100 cm. Very much more must have been lost between the source itself and the 40 cm. distance, since in this region the values of ${}_n\Omega_E$ are necessarily greater.

As an illustration of the way in which measured values of ${}_n\Omega_E$ might be applied to practical problems and as a check on the reliability of the method of interpretation of the observations the transmission efficiency between distances of 40 and 100 cm. may be calculated from the curve shown in fig. 3.

The boundary conditions are defined as an intensity of $4 \cdot 43 \times 10^{-4}$ ergs per sq. cm. per second at a distance of 100 cm. from the source and a frequency of 100 v/sec. (It may be noted that this is the type of *datum* which would be obtained from the practical testing of an actual source.)

Re-writing equation (i) above in the form

$$\frac{dE}{dr} + \frac{2E}{r} + n\,{}_n\Omega_E \,.\, E = 0, \tag{iii}$$

we obtain a differential equation which does not appear to be soluble except as an infinite series so long as the form of the function of Ω with respect to E remains unspecified.

If, however, a curve be constructed from the experimental data between $\log \Omega$ and $\log E$, it is found to be substantially linear for values of E within the range investigated. We may therefore write

$$\log\ \Omega = \log a + p \log E. \tag{iv}$$

From (iii) therefore

$$\frac{dE}{dr} + \frac{2E}{r} + na\,E_{p+1} = 0. \tag{v}$$

The primitive of this is

$$E^{-p} e^{\int -\frac{2p dr}{r}} = C + \int nap e^{\int -\frac{2p dr}{r}} dr \tag{vi}$$

where C is an arbitrary constant.

Whence $$\frac{1}{(\mathrm{E}r^2)^p} = \mathrm{C} - \frac{nap}{2\,p-1} \cdot r^{1-2p}. \qquad \text{(vii)}$$

In the particular case here considered the values of "p" and "a" were obtained from the values of log Ω and log E by the method of Least Squares, assuming the relation between these two variables to be linear and were found to be 1·58 and $5{\cdot}64 \times 10^4$ grams$^{-1\cdot58}$, seconds$^{3\cdot74}$.

From these and the boundary conditions specified the value of C was determined, whence the intensity for a distance of 40 cm. from the source was calculated to be $2{\cdot}58 \times 10^{-3}$ ergs per sq. cm. per second. This shows a calculated transmission efficiency of 0·83, which may be compared with the observed value of 0·845 given above. The close agreement between these two values indicates that the form of the curve relating Ω and E is very approximately accurate for the range which it covers, and that no appreciable error has been introduced in the method of deducing the values of Ω from the experimental observations.

The very small discrepancy between the observed and calculated transmission efficiencies is the more noteworthy since the former was obtained by direct observations and the latter was deduced by a purely mathematical analysis depending on the form of a curve which had itself been obtained by graphical methods from the original measurements. This also provides a certain measure of positive evidence in favour of the contention that the Degradation Coefficient depends only on the energy flux.

The practical application of the foregoing to actual problems of acoustical engineering is obvious, for it follows that one of the essentials for the efficient production of sound is the avoidance, as far as possible, of a high intensity at any point within the system.

In conclusion, it may be pointed out that even if the assumption on which the calculation of the values of $_{100}\Omega$ was based is held to be inadmissible, the experimental proof of the invalidity in this case of the ordinary pressure-distance relation is still of considerable interest. For even if it be contended that this invalidity is wholly due to the fact that the amplitudes involved were not indefinitely small, the experiment still enables a value to be assigned to a lower limit of pressure amplitudes above which the deviations from the normal pressure-intensity relation are no longer negligible for practical purposes.

This is of interest in view of the considerable uncertainty which usually characterises the use of the term "small" amplitudes.

Particles of Long Range Emitted by the Active Deposits of Radium, Thorium and Actinium.

By L. F. Bates, B.Sc., Trinity College, Cambridge, and J. S. Rogers, B.A., M.Sc., Trinity College, 1851 Research Student of the University of Melbourne.

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1. *Introduction.*

For a considerable time after the discovery of radio-activity, it was thought that all the α-rays emitted by a given substance possessed a definite velocity and hence a definite range. It was shown, however, by Hahn,* in 1906, that the active deposit of thorium emitted two distinct sets of α-rays with ranges 4·8 and 8·6 cm. respectively. Although these were at first thought to arise from successive products, it was subsequently established that they were the result of two different methods of the disintegration of the parent atom, thorium C. Marsden and Barratt† were able to show that when thorium C breaks up, 65 per cent. of the atoms contribute α-rays of the longer range and 35 per cent. of the shorter. In 1911, Fajans,‡ in investigating the recoil atoms from radium active deposit, discovered a new product radium C″ which had a half-value period of 1·38 minutes. The fraction of the radium C atoms, which disintegrated with the formation of this product, was found to be only 3 in 10,000. In 1914, Marsden and Perkins§ discovered that actinium C emitted a small number of particles whose range was 6·4 cm. This was followed in 1916 by Rutherford and Wood's‖ discovery of a few particles of range

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* Hahn, 'Phil. Mag.,' vol. 11, p. 793 (1906).

† Marsden and Barratt, 'Proc. Phys. Soc.,' vol. 24, p. 50 (1911).

‡ Fajans, 'Phys. Zeit.,' vol. 12, p. 369 (1911).

§ Marsden and Perkins, 'Phil. Mag.,' vol. 27, p. 690 (1914).

‖ Rutherford and Wood, 'Phil. Mag.,' vol. 31, p. 379 (1916).

11·3 cm. from thorium active deposit, and finally in 1919 Rutherford* established the presence of particles of range 9·0 cm. from radium active deposit. It will be noticed that, in all these cases except the first cited, the large majority of the atoms break up in what might be termed the "normal" manner, while comparatively few produce α-rays of range different from the normal range.

The above results suggested that perhaps the various active deposits emitted, in even smaller numbers, other particles of definite ranges, and a thorough search was undertaken by means of the scintillation method for particles of long range, advantage being taken of the great improvements which have recently been achieved in the methods of counting α-particles. These methods involve the use of microscopes specially designed to increase the brightness of the scintillations observed and in particular to increase the area of the zinc sulphide screen, and consequently the number of scintillations, under observation. The microscope used in the present research was of the type described by Rutherford and Chadwick,† with a holoscopic objective of numerical aperture 04·5 and 16 mm. focal length, together with a specially constructed eye-piece consisting of two large plano-convex lenses and a smaller double convex eye-lens. The field of view was about 20 sq. mm. in area, whilst the fields formerly employed rarely exceeded 3 sq. mm. We have thus been able without greatly increasing the intensity of the radioactive sources to detect the presence of several groups of particles from the active deposits of radium and thorium which had previously not been observed.

2. *Experimental Arrangements.*

The usual procedure was to fix the source in position and then to count the number of scintillations when mica screens of varied stopping powers were interposed between the source and the zinc sulphide screen. One advantage of using such mica screens was that, when only weak sources were available, these could be placed very close to the zinc sulphide screen. Eight counts each of one minute duration were taken with each screen in position. These numbers were then corrected for "contamination" or natural effect, which was measured by noting the number of scintillations still present when the source was removed. Then these numbers, due actually to the radiations from the source, were further corrected for the known decay of the particular active deposit under consideration. To obtain the range, the total "corrected" number of particles, counted for each screen, was plotted against the equivalent air gap, *i.e.*, the distance of the source from the screen plus the calibrated stopping power of the screen in question, all air gaps being found with regard to the standard conditions 15° C. and a pressure of 760 mm. of mercury.

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* Rutherford, 'Phil. Mag.,' vol. 37, p. 515 (1919).

† Rutherford and Chadwick, 'Phil. Mag.,' vol. 42, p. 809 (1921).

The general scheme of the apparatus is indicated in fig. 1. The deposit was formed on a small metal disc D which was screwed into the end of the horizontal brass rod R. The latter was attached to the carrier of a reading microscope so that the source could be placed at any required distance from the zinc sulphide screen Z, which was mounted on a brass frame. Twelve holes, each about 1·3 cm. in diameter, were made in the wheel A, and eleven of these holes were covered with pieces of mica of known stopping powers. The wheel was so mounted that each piece of mica could, in turn, be rotated into position between the source and the screen Z. A light brass spring pressing on the cog-wheel B, mounted on the axle of A, served to fix the latter in definite positions. The number of cogs corresponded to the number of holes in A, and as the wheel was rotated and a fresh mica screen came into position before the screen Z, the spring "clicked," and it was thus possible readily to adjust the different screens in the darkened room. The wheel A was made of thin sheet brass and the mica could be placed so close to the screen Z that the source could be brought within 2 mm. of the screen. The pieces of mica were carefully selected and calibrated in position. A source coated with a deposit of thorium B + C was used for this purpose; the stopping power of each piece of mica was determined from the difference in the positions of the source when the α-rays of range 8·6 cm. just failed to produce scintillations, firstly, when the mica was in position, and secondly when the screen Z was uncovered. In this way it was possible to determine the stopping powers to within 0·1 mm.

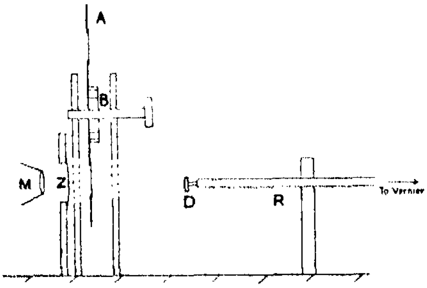

Fig. 1.

With the large field of view of the microscope already described, there was a certain amount of distortion, but the zinc sulphide was attached to the convex surface of a piece of watch glass of suitably large radius of curvature, so that with the exception of a small central portion the whole field was distinctly in focus, and even in this central portion scintillations could be readily detected.

3. *Long-Range Particles from Radium B + C.*

The source of radium active deposit was obtained by exposing a small brass disc, connected to the negative pole of a 200-volt battery, in radium emanation for about 2 hours. The disc was then washed in alcohol and heated in an electric furnace in order as far as possible to remove traces of emanation still adhering to the disc. It is known that the rate of decay of radium active deposit so formed is irregular after long periods have elapsed subsequent to its removal from the emanation, so that in order to check the rate of decay of the sources used, a γ-ray electroscope was set up quite close to the apparatus and the activity of the source was measured several times during each experiment. Usually, the decay was found to be regular for periods not greater than 2½ hours, *i.e.*, in agreement with the values given by Rutherford.* After longer periods the source was usually more active than was to be expected from these values. Experiments were therefore confined to a period of about 2 hours from the time of the removal of the disc from the emanation. The initial γ-ray activities of the sources used varied between those equivalent to 1·5 to 7·0 milligrams of radium.

Experiments in Air : (a) Particles of Range 9·3 *cm.*—The first experiments with these sources were made to investigate the particles of range about 9 cm. previously recorded by Rutherford.† The use of powerful sources with the attendant emission of large quantities of β- and γ-rays caused a certain troublesome luminosity of the zinc sulphide screen, and in the later experiments an electromagnet was used to deflect the β-rays. The disc was placed between 2·5 and 4·5 cm. from the screen. Curves I and II show typical curves obtained with and without the magnetic field, the ranges found from these curves being 9·30 and 9·25 cm. respectively. From thirteen such curves the range was found to be 9·30 ± 0·05 cm. These curves were obtained under different conditions, as with the different positions of the source, different mica screens were used to obtain the end of the range in the various determinations.

To obtain the number of the particles of range 9·3 cm. relative to those of range 6·97 cm. emitted by radium C, the number of the former was determined from similar curves to Curve I by subtracting the number of particles found for a gap of approximately 9·4 cm. from the number for a gap of approximately 7·0 cm., whilst the number of 6·97 cm. α-rays was determined directly by the rotating wheel and slit method,* when these particles passed through an equivalent air gap of 4·7 cm. In this way both the 9·3 and the 6·97 cm. particles had the same residual range, and hence produced scintillations of the same brightness when they struck the zinc sulphide screen. The mean of six determinations showed that the 9·3 cm. particles were present to the extent of 0·0038 ± 0·0005 per cent. of the 6·97 cm. α-rays.

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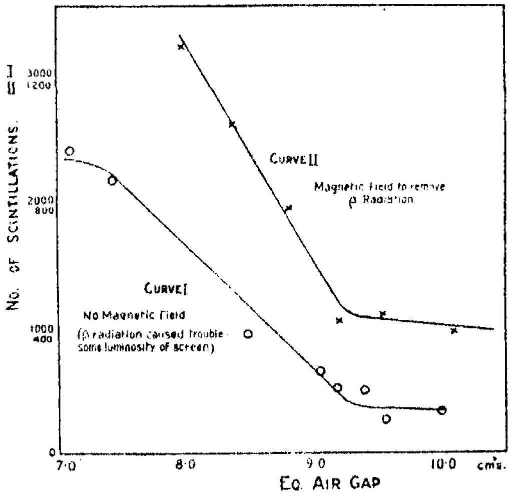
* Rutherford, 'Radioactive Substances,' p. 499.

† Rutherford, *loc. cit.*



Curves I and II.—Radium active deposit.—Particles of range 9·30 cm.

(*b*) *Particles of Range* 11·2 *and* 13·3 *cm.*—The brightness of the scintillations of the particles of range greater than 9·3 cm. and the shape of curves similar to I and II for equivalent air gaps greater than 9·5 cm., suggested that there were present α-rays of still greater range. An extensive examination of these remaining particles was therefore made with the apparatus already described, and, when necessary, an extra mica sheet of 3·76 cm. stopping power was placed between the source and the other screens. More powerful sources, varying in γ-ray activity up to the equivalent of 13 milligrams of radium, were employed and an electromagnet was used to deflect the β-rays. Preliminary experiments showed that these long-range particles could be separated into two groups which appeared to possess ranges of about 11 and 13·5 cm. respectively. Accordingly, the former group was first investigated and Curve III represents the result of a typical determination. In this case the initial γ-ray activity of the source was equivalent to 9·5 mgs. of radium, and it was placed 5·90 cm. from the zinc sulphide. The range found from this curve was 11·2 cm.; in general these results had to be corrected, as the mica screen of stopping power 3·76 cm. mentioned above, was calibrated with only a very short air space between it and the zinc sulphide screen. Now the results of Marsden and Richardson* show that the stopping power of a given piece of mica depends on the emergent range of the α-rays used in its calibration. Their results were therefore used to apply corrections when two or more mica screens were employed simultaneously. It may be added that the largest correction that had to be applied was 2 mm. in the case of radium and 4 mm. in the case of thorium active deposits. The range found from seven curves similar to III was 11·2 ± 0·1 cm.

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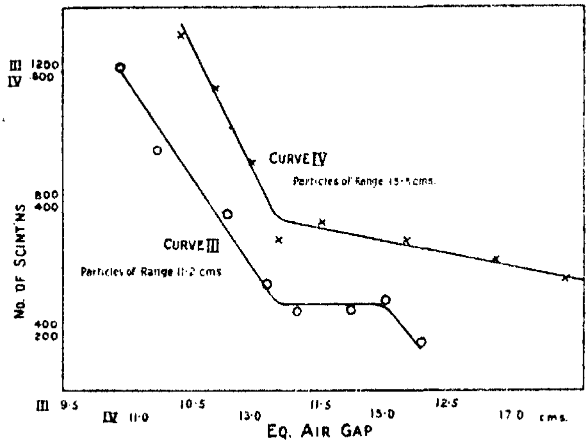
* Chadwick, 'Phil. Mag.,' vol. 40, p. 739 (1920).



Curves III and IV.—Radium active deposit.

The remaining particles of range greater than 11·2 cm. were then examined, and Curve IV shows a typical result. In this case the initial γ-ray activity was equal to 9·15 mgs. of radium, the source was at 7·41 cm. from the screen and the range was found to be 13·3 cm. From six such curves the mean range was found to be 13·3 ± 0·2 cm. It will be seen from Curve IV that beyond equivalent air gaps of 13·5 cm. the number of scintillations gradually decreased, and the remaining particles were not investigated beyond a range of 18 cm., as their appearance, in addition to the shape of the curves, suggested that they were H-particles of long and varied ranges, either emitted by the source or excited by the passage of the α-rays through the air.

To obtain the relative numbers of the long range particles described above in terms of the α-rays of range 6·97 cm. emitted by radium C, the source was fixed in position and the scintillations with equivalent air gaps between the source and screen of (*a*) 13·5 cm., (*b*) 11·6 cm., (*c*) 9·4 cm., and (*d*) 7·5 cm. respectively. The difference between the numbers with gaps (*a*) and (*b*) gave the number of 13·3 cm. particles, the difference with (*b*) and (*c*) the number of 11·2 cm. particles, and that with (*c*) and (*d*) the number of 9·3 cm. particles, the relative number of the latter with respect to the α-rays of range 6·97 cm. already being known. Table I gives the results of six such determinations, the figures in each column representing the total corrected number of scintillations for twelve counts each of one minute duration.

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* Marsden and Richardson, 'Phil. Mag.,' vol. 25, p. 184 (1913).

Table I.—Relative Numbers of Particles of Ranges 9·3, 11·2 and 13·3 cm.

Gap (*a*).	Gap (*b*).	Gap (*c*).	Gap (*d*).
390	647	999	1894
754	918	1461	3258
491	753	1029	2297
448	633	1042	1897
1126	1493	2386	5320
339	487	771	1294
3548	4931	7688	15960

Table IA.

Range of Particles.	Over 13·3 cm.	13·3 cm.	11·2 cm.	9·3 cm.
Number	3548	1383	2757	8272

Finally, therefore, from Table IA it follows that for every 10^7 α-rays of range 6·97 cm. emitted by radium active deposit, there are also emitted approximately 380, 125 and 64 particles of ranges 9·3, 11·2, and 13·3 cm. respectively, together with about 160 long-range H-particles. This last number of course depends on the relative position of the source and screen, as the numbers include those H-particles excited by the 6·97 cm. α-rays both in the air and in the mica screens.

It has been shown above that two new sets of particles of definite ranges have been obtained by employing sources of radium B + C. The question now arose whether these particles were emitted by the active deposit itself or whether they were products of disintegration caused by the passage of α-rays through matter. The brightness of the scintillations suggested that they were α-rays, and the question would of course be settled if electrical and magnetic deflections proved them to be such. However, their numbers were so small that this method would be extremely difficult to apply, and the question had therefore to be settled as far as possible by other means. In the first place, in the case of the 13·3 cm. particles, four of the six determinations of the range were made with the source at least 7 cm. from the mica screens, and therefore no recoil atoms could have been excited in the mica. Four experiments on the 11·2 cm. particles were carried out with the source about 5 cm. from the screens, and here again, as the main beam of α-rays had only an effective range equivalent to 2 cm. of air in the mica, the number of recoil atoms producing scintillations must have been very small. It was, however, quite possible that the main body of α-rays in passing through the air might have produced long-range particles by disintegrating the air molecules, and to test this point the experiments on the two groups of particles were repeated in carbon dioxide.

Experiments in Carbon Dioxide.—An apparatus, fig. 2, similar to one previously used by Rutherford, was employed. Two side tubes T_1 and T_2 were attached to a hollow brass cylinder. One end of the cylinder was closed by a brass cover through which a small piece of brass tubing P passed parallel to the axis of the cylinder; the other was covered by a brass cover in which was a hole about 1·5 cm. in diameter, the centre of which was opposite to the end of the tube P. This hole was covered by a sheet of mica of about 1 cm. stopping power. Just outside the hole a zinc sulphide screen was fixed on a small bracket, so that pieces of mica V of various stopping powers could be placed before the screen. The source D was screwed into the end of a brass rod which slid tightly in the tube P. The rod was coated with thick grease and when it was pushed into position, the apparatus was airtight. The apparatus was placed between the poles of an electromagnet, and a slow stream of dry carbon dioxide was maintained in the cylinder during the experiment to remove any emanation in the cylinder. In spite of this precaution a certain amount of trouble was caused by the presence of small amounts of emanation. With the experiments in air this trouble was not experienced, as air was continuously withdrawn from the immediate neighbourhood of the source by means of a water pump.

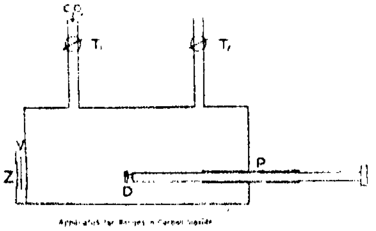

FIG. 2.

The source was always placed more than 5 cm. from the first piece of mica, and as the stopping power of carbon dioxide is 1·48 times that of air, none of the α-rays of range 6·97 cm. reached any mica. From three determinations the range of one set of particles was found to be 11·3 ± 0·2 cm., and from four experiments the range of the other set was 13·6 ± 0·2 cm. The agreement with the results in air is considered good in view of the greater experimental difficulties. It was therefore concluded that the particles measured were emitted by the source. It may be added that the number of particles of range greater than that of the longer particles here measured was less when the experiments were carried out in carbon dioxide than in air.

Experiments with the Active Deposit formed on Platinum.—There still remained the possibility that the particles measured were excited in the brass disc itself. A deposit was therefore formed on a disc of platinum foil and this was used as a source in air. A cursory examination showed that the particles were still present, and the determination of the range of one group gave 11·3 cm.

4. *Long-Range Particles from Thorium B + C and Thorium C.*

Particles of Range 11·5 *cm.*—The first experiments with these sources were made to confirm the range and the relative numbers of the rays previously found by Rutherford and Wood.[*] A source of thorium C was obtained by continuously rotating a nickel disc, the back of which was coated with shellac, in a hot solution of radiothorium, and this disc after being washed with distilled water was mounted in the apparatus already described. As the sources available were comparatively weak, the disc had to be placed about 2·5 cm. from the zinc sulphide screen, and in order to obtain the necessary equivalent air gaps, extra mica screens were placed between the source and the wheel A (fig. 1). (This arrangement had the disadvantage that it allowed the 8·6 cm. α-rays to strike the mica with sufficient energy to eject particles; this will be evident from the large number of H-particles in Table IVA.) As the stopping powers of these extra screens were determined as before, a correction in accordance with the results of Marsden and Richardson[†] had to be applied to the ranges found from the curves. Curve V shows the result of a typical experiment; here the deposit was obtained by immersing the nickel disc in the solution for 15 minutes, and the source was placed 2·26 cm. from the zinc sulphide. From four such curves the range was found to be 11·5 ± 0·05 cm., a result which is in agreement with that of Rutherford and Wood.

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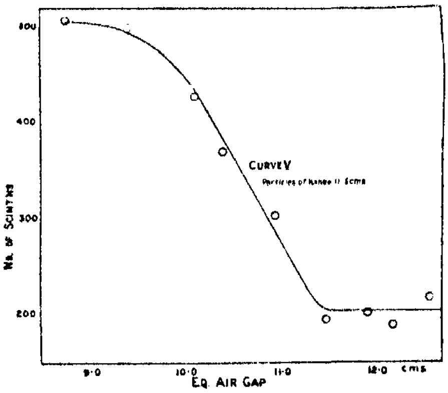
[*] Rutherford and Wood, *loc. cit.*

[†] Marsden and Richardson, *loc. cit.*

Unfortunately, in these experiments it was found that thorium X was always deposited on the nickel disc, and produced so much emanation that, in spite of the continuous removal of the air near the source by a water pump, a troublesome contamination was caused. Although the radiothorium solution was re-made by precipitating the radiothorium with excess ammonium hydroxide and redissolving the precipitate in hydrochloric acid, it was found impossible to obtain a source of thorium C really free from thorium X. In all further work the active disc was therefore screwed into a subsidiary brass holder over which a short brass tube could be placed. One end of this tube was closed by a thin sheet of mica which almost touched the disc, and the other end was attached to the holder with soft wax, *i.e.*, the source was covered with an airtight cap.



Curve V.—Thorium active deposit.

Ratio of the Numbers of α-Rays of Ranges 11·5 and 8·6 *cm.*—The relative number of the 11·5 cm. rays with respect to that of range 8·6 cm. was obtained by counting the number of scintillations which appeared with equivalent air gaps of approximately 11·6, 9·0 and 6·5 cm. respectively, a rotating wheel and slit being used on the last gap. The difference between the corrected numbers on the first and second gaps gave the number of 11·5 cm. α-rays, whilst the corrected number on the last gap gave the number of 8·6 cm. α-rays. The effective diameter of the rotating wheel was 11·56 cm. and several different slits were used. The results of five determinations are given in Table II., the last column of which gives the relative numbers of the two sets of particles.

Table II.—Relative Numbers of 8·6 and 11·5 cm. α-Particles.
(Source :—Thorium C.)

1st Gap.	2nd Gap.	3rd Gap.	Slit Width (mm.).	Percentage.
442	550	2544	1·65	0·0228
935	5736	4503	0·073	0·0212
316	1304	1685	0·100	0·0162*
272	979	1467	0·173	0·0230
354	1164	1872	0·173	0·0206
			Mean Percentage	0·021

* This percentage has only been given half-weight, as a large contamination was observed during the experiment.

It would have been interesting to check these percentages by obtaining the initial number of 8·6 cm. α-rays in a different way, viz., by allowing the source to decay until it was possible to count the number of these α-rays emitted, and then obtaining the initial number from the known rate of decay of thorium C. Unfortunately, the presence of thorium X rendered such experiments futile, as the thorium emanation formed an active deposit on the source and its surroundings.

The percentage was also obtained in a similar manner using sources of thorium B + C deposited on a negatively charged brass disc by prolonged exposure to thorium emanation. Unfortunately, these deposits were rather weak ; the results of the experiments are given in Table III.

Table III.—Relative Numbers of 8·6 and 11·5 cm. α-Particles.
(Source :—Thorium B + C.)

1st Gap.	2nd Gap.	3rd Gap.	Slit Width (mm.).	Percentage.
261	436	966	0·404	0·0202
275	538	1066	0·397	0·0270
189	383	883	0·397	0·0241
			Mean Percentage	0·024

The mean values of the percentages from Tables II and III do not agree with the value given by Wood,† which was approximately 0·01 per cent. This experimenter employed sources of thorium B + C, and, after counting the scintillations due to the 11·5 cm. rays, allowed the source to decay *in situ* until the number of scintillations produced by the 8·6 cm. α-rays was of the same order as that in the earlier part of the determination; the initial number was then calculated from the known rate of decay of thorium B. In all the above experiments the latter number was found by the rotating wheel and slit method, and it was thought probable that some irregularity in the rate of decay of thorium B might have caused the discrepancy between Wood's result and that given in this paper. Some measurements were therefore made in which Wood's procedure was followed. In the first three experiments deposits of thorium B + C on brass discs were used, and the following percentages were obtained:—0·160, 0·0330 and 0·0990. It was considered that the last value was excessively high owing to the oxidation of the brass surface on which the active deposit had decayed for four days, and two more values were obtained with the deposits on aluminium discs. These values were 0·0224 and 0·0322. Omitting the discredited value 0·099, the mean value is 0·026. The larger variation among the individual determinations, than among those in Tables II and III, might partly be attributed to changes in the active surface during the long period of decay, and partly to the smaller numbers, and hence larger probability variations of the 11·5 cm. particles and those of still longer range. These results show, however, that the discrepancy cannot be referred to an irregularity in the rate of decay of thorium B.

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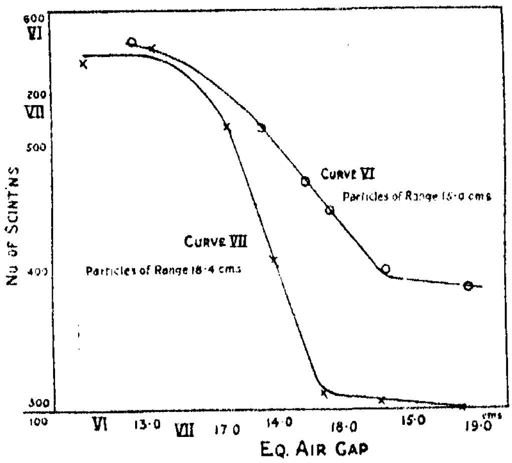
† Wood, 'Phil. Mag.,' vol. 41, p. 575 (1921).

Particles of Ranges 15·0 *and* 18·4 *cm.*—An examination of the remaining particles showed that there were present two further groups with definite ranges. Curve VI shows a determination of the range of the shorter group. In this experiment the source was only 1·85 cm. from the screen, and the



Curves VI and VII.—Thorium active deposit.

range corrected in accordance with the results of Marsden and Richardson was found to be 15·1 cm. The source had to be placed so close to the screen because the initial γ-ray activity of the source, as measured by the activity of the thorium D produced, was only of the order of 0·2 mgs. of radium. Five determinations fixed the range at 15·0 ± 0·2 cm. As it was desirable to verify this value with an intense source situated much further from the screen, through the kindness of Sir E. Rutherford, one was obtained equal in γ-ray activity to 1·04 mgs. of radium. This was placed 5·55 cm. from the screen and the range was found to be 15·1 cm.

The remaining group of particles was similarly examined, and from four determinations with weak sources their range was established at 18·4 ± 0·2 cm. Curve VII illustrates the result of one experiment where the source was placed 1·71 cm. from the screen, the range being 18·2 cm. As before, one intense source was procured, in this instance of 1·27 mgs. activity. From this source, placed at a distance of 5·57 cm. from the zinc sulphide screen, a range of 18·3 cm. was obtained.

The activity of the sources of thorium C available was considered too small to permit any further accurate investigation of the particles of range longer than 18·5 cm. However, it seemed unlikely from the appearance of the scintillations that any particles other than H-particles were present.

The relative numbers of these long-range particles were determined in the manner previously described, by counting the numbers of scintillations with equivalent air gaps of 18·5, 15·4, 12·0 and 8·7 cm. respectively. Four such experiments were carried out and at each gap there were taken twenty counts each of one minute duration. The results are set out in Table IV.

Table IV.—Relative Numbers of Particles of Ranges 11·5, 15·0 and 18·4 cm.

1st Gap.	2nd Gap.	3rd Gap.	4th Gap.
92	748	1030	2058
190	306	410	941
199	431	568	1432
149	272	383	893
1030	1757	2391	5324

Table IVa.

Range of Particles............	Over 18·5 cm.	18·4 cm.	15·0 cm.	11·5 cm.
Number	1030	727	624	2933

In Table IVA are given the numbers, found from Table IV, of the particles of the different ranges. If the number of the 11·5 cm. α-rays are taken as 0·0220 per cent. of the number of 8·6 cm α-rays (a value obtained by giving the mean percentage of Table II twice the weight of that of Table III), then for every 10^6 α-rays emitted by thorium C there are emitted 220, 47 and 55 particles of ranges 11·5, 15·0 and 18·4 cm. respectively, together with about 77 particles, the number of which depends on the experimental arrangement used, and which are probably long-range H-particles.

5. *Long-Range Particles from Actinium B + C.*

Particles of Range 6·49 *cm.*—The first experiments with sources of actinium B + C were made to verify the ranges and relative number of the particles discovered by Marsden and Perkins.* The amount of actinium salt available was not large and the apparatus shown in fig. 3 was used in the hope of obtaining the most intense active deposit possible on a small surface. The small brass disc D, which varied in different experiments from 2 to 4 mm. in diameter, was screwed into the brass rod *r* and connected to the negative terminal of the 200-volt direct current supply. The rod *r* was insulated from the brass tube T by ebonite plugs and the ebonite stopper S. T was in electrical connection with the walls of the vessel V and the positive terminal of the current supply. The actinium salt was spread on the bottom of the vessel V, and as the lower surface of D was the only negatively charged surface exposed within the vessel, it was expected that the maximum active deposit would be formed on D. It was found later, however, that by removing the tube T and by covering the upper surface of D and the rod *r* with sealing wax, sources about fifteen times as intense could be secured. Apparently, the positively charged tube repelled many of the positively charged particles and prevented them from reaching D.

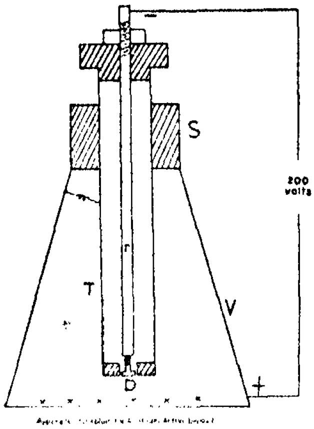


FIG. 3.

(*a*) *Determination of the Range.*—The range was found as in the preceding sections, with the exception that a slight trace of thorium present with the actinium salt necessitated a modification in the method in obtaining the contamination effect. The number of α-rays arising from the presence of the thorium active deposit on the disc D was obtained by counting the number of scintillations due to particles which passed through an equivalent air gap greater than 6·5 cm. two hours after the removal of the source from V, after which period the number of particles of range greater than 6·5 cm. from actinium itself was negligible. The initial number of thorium particles rarely exceeded 2 per minute.

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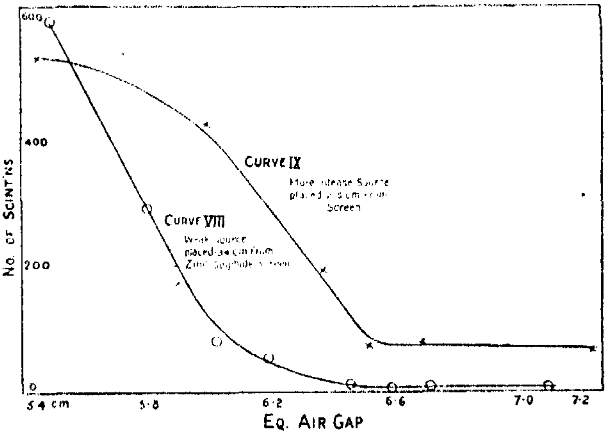
* Marsden and Perkins, *loc. cit.*

Curve VIII is an example of the determination of the range with the weaker sources. These sources had to be placed very close to the zinc sulphide screen—at distances varying from 2 to 5 mm. For the curve shown this distance was 3·4 mm. and the initial number of α-rays due to thorium was 1·6 per minute. The shape of the curve was greatly influenced by the closeness of source and screen. This is evident from the absence of the usual straight descent almost to the end of the range. It was a matter of some difficulty to determine the range accurately from this curve. It would be expected that the curve would cut the air gap axis at a point corresponding to the end of the range. It will be observed that the curve does not intersect the axis but runs parallel to it beyond the point 6·5 cm. (approx.). The point where the curve commenced to run parallel to the axis was taken as the range. The range from Curve VIII was found to be 6·49 cm., and the mean range from eight determinations was 6·49 ± 0·02 cm.



Curves VIII and IX.—Actinium active deposit.—Particles of range 6·49 cm.

The stronger sources were placed much further from the screen and hence curves similar to Curve IX were produced. For this curve the source was 2·60 cm. from the screen and the range was 6·47 cm. From three such curves the mean value of the range was 6·50 ± 0·02 cm., no more determinations being made as the agreement with the previous values was so satisfactory. The respective values of the range found by Marsden and Perkins and by Varder and Marsden* were 6·4 and 6·5 cm.

It was shown in the following manner that the number of particles of this range decreased with the period of actinium active deposit. A mica screen of sufficient stopping power was inserted so that no particle of range less than 5·5 cm. struck the screen. The numbers of particles counted were then corrected, and the total numbers for each successive eight counts were found to be constant within the limit of experimental error.

(*b*) *Relative Number of the α-Rays of Ranges* 5·5 *and* 6·5 *cm.*—With the weaker sources the ratio of the number of 6·5 cm. particles to that of the total number of α-rays emitted by actinium C was obtained by counting the numbers of scintillations with equivalent air gaps of 5·5 and 4·5 cm. between source and screen, the position of the source being fixed. For the greater gap the particles of range 6·5 cm. only were able to strike the screen, while the smaller gap allowed particles of both ranges. In order to reduce the numbers with the second gap sufficiently for accurate counting, the source was allowed to decay *in situ* for six hours after its removal from the vessel V. Here again the disadvantage of a non-parallel beam of rays was apparent, because the angles of the cones of rays reaching the screen from a given part of the source differed for the two groups of rays. Six determinations of the ratio gave a mean value of 0·41 per cent. This value must be regarded as an upper limit, as the angle of the cone of rays for the shorter range particles was reduced to a greater extent than that for the longer, and further no allowance was made for particles excited in the air and mica.

More reliable values were obtained with the more intense sources. Again the numbers of scintillations were counted with equivalent air gaps of roughly 5·5 and 4·5 cm., the actual gaps always differing exactly by 1 cm. Instead of allowing the source to decay for a long period, the number of particles for the shorter gap was obtained by the wheel and slit method. This method at once reduces any error due to uncertainty in the rate of decay of the source for long periods. Table V gives five determinations of the ratio, and for each gap in all these experiments twenty counts each of one minute duration were taken, in addition to counts to correct for the contamination of the zinc sulphide screen. As far as possible, different mica screens to supply the necessary air gaps and different slits for the wheel were used in order to reduce any errors arising from possible irregularities in either mica or slits.

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[*] Varder and Marsden, 'Phil. Mag.,' vol. 28, p. 818 (1914).

Table V.—Ratio of No. 6·5 cm. Rays to Total Number of α-Rays from Actinium C.

Distance Source to Screen.	Slit Width.	Ratio (Percentage).
cm.	mms.	
4·63	2·86	0·347
2·93	2·86	0·334
4·63	3·68	0·301
2·93	2·87	0·314
4·64	3·68	0·315
	Mean	0·322 ± 0·015*

* In this value no correction has been made for particles of range greater than 6·5 cm., mentioned below. The mean percentage corrected for such particles is **0·296**.

The agreement between the different results is very satisfactory. The mean value here given differs considerably from that of Marsden and Perkins, who found a value of about 0·15 per cent. This lack of agreement is attributed partly to the fact that these authors had less satisfactory optical arrangements and partly to the manner in which they obtained the total number of α-rays emitted.

Particles of Range greater than 6·5 cm.—It will have been seen from Curves VIII and IX that there were present particles of range greater than 6·5 cm. Curves similar to IX showed that the number of such particles was about 0·026 per cent. of the total number of α-rays emitted by actinium C. This number would, however, include H-particles excited by the 5·5 cm. particles in the air and mica. Attempts were made to secure sufficiently intense sources to investigate these long-range particles, but even with the most intense source placed 5 mm. from the screen, the number of particles of both types exclusive of contamination amounted to about 10 per minute. In view of the quick rate of decay of this active deposit, such small numbers were insufficient for any range determination. Again, although quite bright scintillations were observed with gaps exceeding 6·5 cm., it was impossible to form any definite conclusions as to their nature from the appearance of the scintillations alone. Although it is considered very likely that α-rays of range exceeding 6·5 cm. are emitted, sources at least five times as intense as those at present at our disposal would be necessary to establish them.

6. *Discussion of Results.*

Before any definite conclusions can be drawn from the discovery of these particles of long range, it will be necessary to prove their nature, *i.e.*, whether they are α-rays or H-particles. It has been stated above that these particles appear from relative brightness to be α-rays. It must be pointed out, however, that this evidence is far from conclusive, as these particles have never been observed alone but always when accompanied by particles of different types, viz., the particles of range longer than 13·3 cm. in the case of radium, and longer than 18·4 cm. in the case of thorium. This means the simultaneous observation of a series of particles whose scintillations vary greatly in brightness, so that it is extremely difficult to concentrate on one set of particles and determine their nature from the brightness of the scintillations. Again, the scintillations produced by a beam of α-rays of equal range vary considerably in brightness; this may be due partly to the fact that all the α-rays do not strike the screen in the same manner, and partly to the fact that all the zinc sulphide crystals are not focussed with equal sharpness in the field of the microscope. On the other hand it must be pointed out that the scintillation method is the only method at present available for investigating these long-range particles, as any attempts to examine them by ionization measurements would fail, owing to the large effects of very fast β-rays and of γ-radiation.

Various authors* have from time to time given schematic representations of the mode of disintegration of the C products of the radioactive substances. Whatever may be the nature of the long-range particles discussed in this paper, it appears that these schemes must be considerably modified. In particular, the existing schemes take no account of the 11·5 cm. particles from thorium C which Rutherford† has definitely proved to be α-rays, and it is clear that the disintegration of the C products is much more complicated than has hitherto been supposed.

The experimental evidence leads to the conclusion that the atoms of radium C and thorium C emit particles of four quite different ranges. The energy differences between these particles can be calculated if it is assumed that they are α-rays.

The velocities of these particles can be obtained from Geiger's rule, $v^3 = a\,\mathrm{R}$, which connects the velocity v and the range R, a being a constant. From these the energies can be calculated, if we take as standards for such calculation the velocity of the 6·97 cm. α-particles to be $1{\cdot}922 \times 10^9$ cm. per second, and the mass of the α-particle to be $6{\cdot}59 \times 10^{-24}$ gm. In Table VI the energy differences between the consecutive ranges are given both in ergs and in volts.

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* Marsden and Perkins, *loc. cit.*; Fajans, 'Phys. Zeit.,' vol. 12, p. 369 (1911), and vol. 14, p. 951 (1913); Marsden and Wilson, 'Nature,' vol. 92, p. 29 (1913).

† Rutherford, 'Phil. Mag.,' vol. 41, p. 570 (1921).

Table VI.—Differences in Energy between Particles of Consecutive Ranges.

(*a*) Radium C.

Range Difference	9·3 — 7·0	11·2 — 9·3	13·3 — 11·2
Energy—			
(i) **Ergs**	$2{\cdot}58 \times 10^{-6}$	$1{\cdot}96 \times 10^{-6}$	$2{\cdot}03 \times 10^{-6}$
(ii) **Volts**	$16{\cdot}2 \times 10^{5}$	$12{\cdot}3 \times 10^{5}$	$12{\cdot}8 \times 10^{5}$

(*b*) Thorium C.

Range Difference	11·5 — 8·6	15·0 — 11·5	18·4 — 15·0
Energy—			
(i) **Ergs**	$2{\cdot}99 \times 10^{-6}$	$3{\cdot}29 \times 10^{-6}$	$2{\cdot}99 \times 10^{-6}$
(ii) **Volts**	$18{\cdot}8 \times 10^{5}$	$20{\cdot}7 \times 10^{5}$	$18{\cdot}8 \times 10^{5}$

With regard to the relative numbers obtained for the two sets of particles of the longest ranges from radium C and thorium C, it must be understood that these numbers can only be regarded as an approximate estimate of the extent to which such particles are present. Any percentage determinations based on scintillation work are obviously subject to probability variations. The latter may be decreased by increasing the number of observations, but this procedure requires protracted series of experiments. Moreover, as the particular percentages under consideration were obtained from the differences between quantities which were themselves open to large experimental errors, their accuracy is correspondingly diminished.

7. *Summary.*

An examination of the long-range particles emitted by the active deposits of radium, thorium and actinium has been made by the scintillation method, advantage being taken of the recent improvements in the microscopes used for observing scintillations.

In the case of radium active deposit, in addition to the particles of range 9·3 cm. previously found by Rutherford, particles of ranges 11·2 and 13·3 cm. have been discovered. The numbers of these three sets of particles are comparatively small; for every 10^7 α-rays emitted by radium C it has been found that there are present 380, 125 and 64 of these particles respectively.

In addition to the particles of range 11·5 cm. discovered by Rutherford and Wood, it has been found that thorium active deposit also emits particles of ranges 15·0 and 18·4 cm., the relative numbers of the 8·6, 11·5, 15·0 and 18·4 cm. particles being 10^6, 220, 47 and 55 respectively.

Actinium active deposit has been found to emit the particles of range 6·49 cm. previously recorded by Marsden and Perkins, to the extent of 0·322 per cent. of the total number of α-rays emitted by actinium C. Indications of the presence of particles of range greater than 6·5 cm. have been found, but it has been impossible to establish them, as the sources at our disposal were insufficiently intense.

The bearing of these new long-range particles upon the modes of representation of the transformation of the C products of the radioactive substances has been discussed, and it is shown that these schemes must be regarded as incomplete. In particular, for the atoms of radium C and thorium C, explanation must be found for the presence of four particles of different ranges.

In conclusion, we wish to express our best thanks to Sir Ernest Rutherford who suggested this research and who gave us many helpful suggestions during its progress, and to Mr. G. A. R. Crowe who prepared for us the sources of radium active deposit.

Further Studies in Ionization: Hydrogen and Oxygen.

By H. D. Smyth, Ph.D., National Research Fellow in Physics, U.S.A.

(Communicated by Prof. Sir E. Rutherford, F.R.S.—Received December 5, 1923.)

Recently the writer* described a new method for studying the ionization of gases by electron impact and presented the results of experiments on nitrogen. Similar data have now been obtained for hydrogen and oxygen and form the subject of the present paper. Both apparatus and procedure were identical with those used in nitrogen and therefore will not be described in detail. But, perhaps, it may be as well to recall that the object of the method is to produce ions under the controlled energy conditions of an ionizing potential experiment and at the same time determine their m/e by positive ray analysis. As to how this is achieved, we shall only say as much as seems necessary to make the results intelligible.

Consider the schematic diagram in fig. 1. By a suitable arrangement of pumps and leaks a fair density of the gas being studied is kept on the left side of the electrode E_2, but this is greatly reduced between E_2 and E_3, and still further on the right of E_3 where the mean free path of an ion must be of the order of 10 cm. Thus, an ion produced in the neighbourhood of E_1 by an electron of speed V_1 from the filament F is accelerated toward E_2 by V_2. If it passes through S_1 it is further accelerated by the large field V_3. Passing on through S_2 into the positive ray box it is bent in a semi-circle by a uniform magnetic field H and reaches an insulated plate connected to an electrometer. By varying H or V_3 ions of different *m/e* are brought on to the plate. In practice, a run is made by keeping V_1, V_2 and H constant and observing the electrometer current as V_3 is varied. In this way the proportions of different types of ion under given conditions of ionization are observed. By comparing runs taken at different values of V_1, the critical potential for each type of ion is found. The results of experiments of this sort on hydrogen and oxygen are given below.

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* 'Roy. Soc. Proc.,' A, vol. 104, pp. 121–134 (1923).

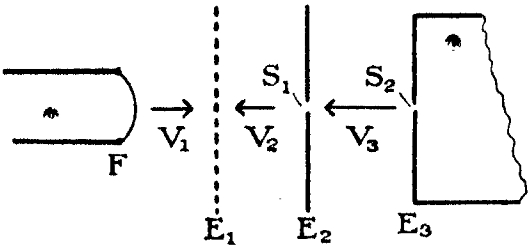

FIG. 1.

PART I.—HYDROGEN.

(*a*) *Experimental Details.*

The nitrogen generator attached in previous experiments was replaced by a palladium tube. Hydrogen admitted through this by the action of a bunsen flame was stored over phosphorus pentoxide and leaked into the ionization tube through a fine capillary. Occasional blank runs covering a region up to about $m/e = 35$ showed water vapour as the only impurity present. As in the previous work, the pressure could not be determined directly, but the McLeod gauge readings, with the pumps connected, and one minute after disconnecting them, are recorded.

(*b*) *Results.*

In fig. 2 a typical run is shown. The *m/e* scale is obtained from the equation

$$m/e = C\,H^2/V$$

where C is a constant determined by the results on nitrogen, H is the magnetic field read from a calibration curve of the magnet and $V = V_2 + V_3$ the voltages observed. The various constants for the run are shown in the caption where i is the current to E_1 and all the other symbols have already been explained.

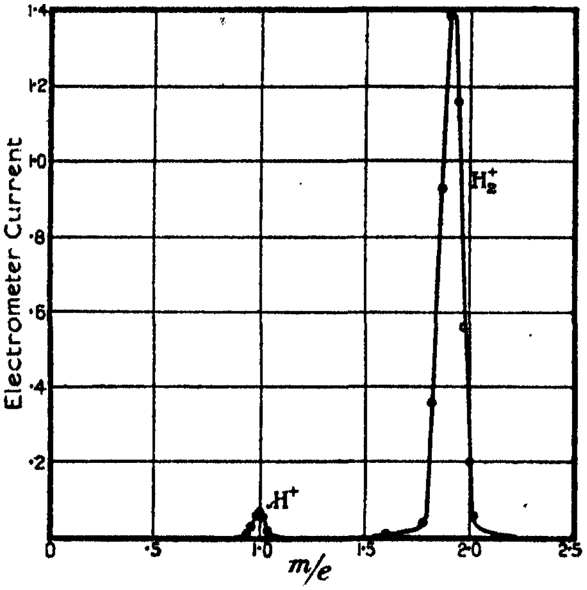

FIG. 2.—$V_1 = 40$; $V_2 = 40$ volts; $H = 1075$ Gauss; $i = 655$ microamps; $p = 0 \cdot 0000 \rightarrow 0 \cdot 0002$ mm.

The surprising feature of the curve is the very small relative intensity of the H^+ peak, suggesting that molecular ionization is not accompanied by dissociation. It was found impossible to reproduce these relative intensities exactly, and no correlation was observed between their variation and that of thermionic current, magnetic field or pressure (within certain limits). However, as in nitrogen, a change of filament had a very great effect. On this account it is impossible to draw more than qualitative conclusions from such evidence, but, if the variation of intensities with V_1 is considered, the results are more definite. Such a curve is shown in fig. 3, where the heights of the H^+ and H_2^+ peaks are plotted against corresponding values of V_1. Apparently, the H_2^+ ions are first formed at 16·5 volts and the H^+ not until 20·7 volts. To check these values for each series of runs, the individual runs at low voltages are considered as well as the ensemble plotted in fig. 3. Thus, in this case, at 17·0 volts a very small but definite peak is found for H_2^+, while there is no trace of one at 16·4, showing the critical potential is between these values. This method of deduction is important in many series where there is a large zero effect, so that the curves do not actually come down to the axis but merely to a zero line none too sharply defined.

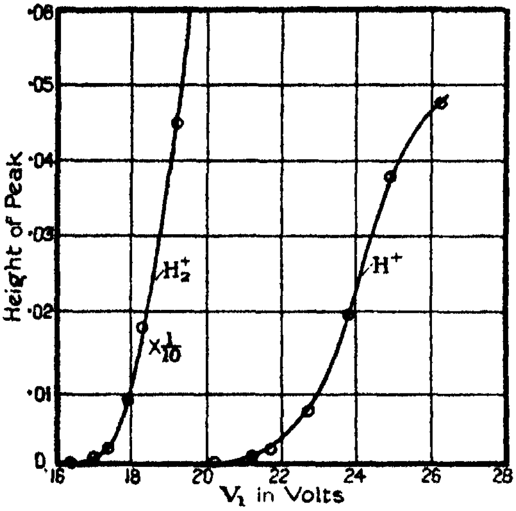

Fig. 3.—Series 8.

The assembled results of these observations are given in Table I.

Table I.—Results on Hydrogen.

Series	Fil.	H	i	$p 10^{-2}$ mm.	Observed Potentials with Weights.		
					$V_{H_2^+}$	V_{H^+}	$V_{H^+} - V_{H_2^+}$
1	I	1080	700–800	0·00 → 0·01	17·5	—	—
2	I	1080	800	—	18	25	—
3	I	1060	800–900	0·01 → 0·22	15·4 (4)	19·8 (4)	4·4 (16)
4	II	730	900	0·03 → 0·12	—	20·5	—
5	II	730	900–800	0·015 → 0·12	16·8 (6)	20·8 (4)	4·0 (24)
6	III	820	700–800	0·01 → 0·22	17·6 (8)	22·3 (5)	4·7 (40)
7	III	840	210	0·02 → 0·28	17·7 (8)	21·6 (3)	3·9 (24)
8	III	840	900–860	0·01 → 0·15	16·5 (10)	20·7 (8)	4·2 (80)
9	III	840	2500	0·01 → 0·15	15·4 (10)	19·6 (5)	4·2 (50)
				Mean Values	—	—	4·25 ± 0·062
10	VI	800	350–500	0·06 0·88	17·1	18·9	1·8
11	VI	800	—	0·42 7·5	17·6	17·5	–0·1

It should be noted that all the voltages given are those observed without correction for initial velocity or potential drop across the filament. This may have varied considerably and presumably accounts for the wide range of observed values of $V_{H_2^+}$ and V_{H^+}. (In particular, for filament III, a bad contact between filament and lead caused a further complication.) But as $V_{H_2^+}$ has been fixed at about 16 by a number of observers with greater accuracy than is possible by this method, no attempt at correction was made and no estimate of the true value is given.

On the other hand, if V_{H^+} is a true critical potential $V_{H_2^+} - V_{H^+}$ should be constant, and if not, $V_{H_2^+} - V_{H^+}$ might vary with filament, with magnetic field, with thermionic current or with pressure. In Nos. 3 to 9 all these factors were varied, three different filaments were used, the magnetic field varied by 30 per cent., the thermionic current by a factor of twelve and the pressure by a factor of two, but the variation of $V_{H_2^+} - V_{H^+}$ was small and apparently purely random. This leads to the conclusion that an electron with a speed between 16·0 and 20·2 will ionize a hydrogen molecule without causing dissociation, but that an electron of a greater speed may cause dissociation simultaneously with ionization.

Before discussing the significance of these results, there are some further experimental points to be mentioned. Firstly as to the variation of intensity with thermionic current, experiments were made at $V_1 = 35$ with i about 900, then with it reduced to 250 and then high again. The ratios of the intensities per unit current at high current to those at low were found to be 1·12 and 1·09 for H^+ and H_2^+ respectively. This indicates an intensity rising a little more rapidly than the first power of the current to E_1 and in the same way for both peaks. Though the small intensities of H^+ made the observations on it rather rough, the conclusion is that both types of ion were produced by single impacts.

Secondly, runs were made with V_1 as high as 600 without any marked effect on the relative intensities of H^+ and H_2^+.

Finally, a search was made for a peak corresponding to H_3^+ but none was found. No attempt was made to study negative ions.

(c) *Discussion.*

In spite of the large number of experiments made on ionization in hydrogen there has not been complete accord as to either the exact value of the critical potential at about 16 volts or its interpretation. The present observations are too inaccurate to help us toward a more exact value, and for convenience 16 volts will be assumed as the true value in this discussion. They do, however, throw light on the questions of interpretation.

Heretofore, there has been a tendency to regard the ionization of molecular hydrogen as accompanied by dissociation, and to identify the difference between atomic and molecular ionization potentials with the heat of dissociation. This point of view is illustrated by the experiments of Olson and Glockler,* who hoped to get an accurate means of calculating the heat of dissociation of hydrogen by measuring its critical potentials.

On the other hand, the discrepancy between the observed differences in critical potentials, two to three volts, and Langmuir's determination of the heat of dissociation, 3·6 volts, inclines Foote and Mohler† to consider that the 16·0 volt critical potential may simply mean the production of molecular ions. Again, von Keussler‡ after considering various spectroscopic data and his own experiments concludes that ionization takes places in two stages. By the electron impact the molecule is excited, and if it collides before radiating it dissociates into a normal atom and one that is ionized, or at least excited.

In the experiments described above the pressure was so low that secondary collisions were very improbable. The conclusion is, therefore, that 16-volt electrons not merely excite but ionize hydrogen molecules, but that no dissociation takes place. If the electrons have 4·25 volts more energy, dissociation may accompany ionization though the relative intensities suggest that it is improbable. This new critical potential at about 20·2 volts does not agree with any previous observations, though Foote and Mohler, as well as Horton and Davies, have found indications of inelastic impacts at about 23 volts. As it corresponds to no increase in the total number of ions but merely to an increase in mobility of some of them, it would hardly be detectable. More fundamental reasons for its absence arise from the suggestions of the following paragraphs.

It may be recalled that von Keussler suggested dissociation as a secondary effect due to the collision of an excited molecule with another molecule. If, then, experiments could be performed which made it probable that the hydrogen ions would suffer collision in the space between E_1 and E_2 we might expect them to be dissociated, and consequently that we should get an increased number of atomic ions. The distance between E_1 and E_2 was 9 mm. and the pressure giving this mean free path in hydrogen is 0·015 mm.

Consider the run shown in fig. 4. The pressure recorded on the McLeod gauge was 0·0042 mm., rising to 0·075 mm. in one minute with the pumps shut off, so that the actual pressure between E_1 and E_2 during the run was between these limits, say 0·02. The relative intensities of H_2^+ and H^+ are completely reversed. Moreover, this run in fig. 4 is but one of the series 11 shown in Table I, where it was found that at this high pressure the H^+ ion persisted to the same voltage as H_2^+. As other experimenters have worked under conditions more like those of this series, it is not surprising that no critical potential at 20·2 has been observed. The runs of series 10, taken at an intermediate pressure, showed H_2^+ still the dominant product, but H^+ persisting to within 1·8 volts of $V_{H_2^+}$ indicating a considerable number of secondary dissociations.

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* A. R. Olson and George Glockler, 'Proc. Nat. Acad. Scien.,' vol. 9, p. 122 (1923).

† Foote and Mohler, 'Origin of Spectra,' p. 76.

‡ V. v. Keussler, 'Zeits. für Phys.,' vol. 14, p. 19 (1923).

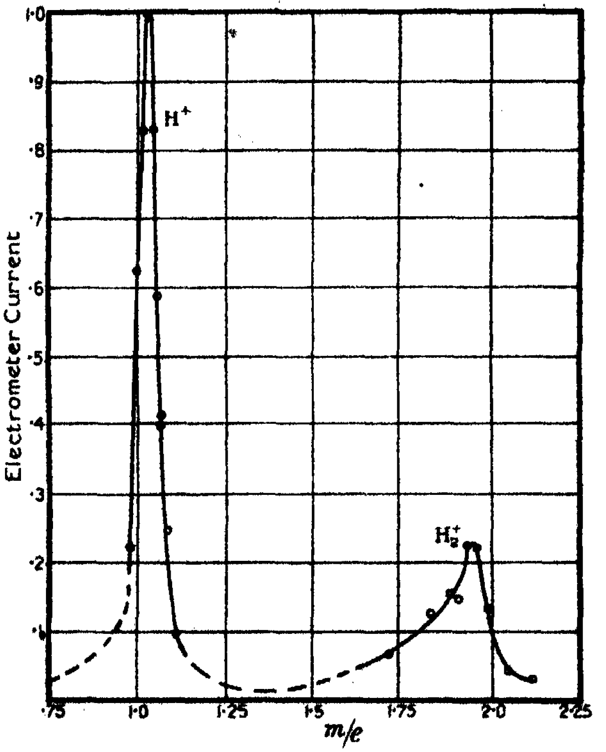

FIG. 4.—$V_1 = 20·7$; $V_2 = 20·7$ volts; $H = 800$ Gauss ; $i = 480$ microamps ; $p = 0·0042 \rightarrow 0·075$ mm.

Unfortunately, these two series of runs were taken about two months after the last of the others and after the tube had been used for oxygen. The only change had been the substitution of a lime-coated platinum filament for the tungsten ones used previously, and there seems no reason why this should have had any effect. Nevertheless, the evidence of series 10 and 11 should be regarded as suggestive rather than conclusive. The writer is setting up an entirely new apparatus with the view of checking the results given here and further investigating this last point concerning the effect of pressure.

PART II.—OXYGEN.

(*a*) *Experimental Details.*

The tungsten filament previously used was replaced by one of platinum strip, lime-coated from a touch of sealing wax. Oxygen was prepared by heating potassium permanganate, then passing it through KOH and P_2O_5. It was stored over P_2O_5 and the previous arrangement of reservoir and leak was used. The compensating magnet, unnecessary in the work on hydrogen, was used again as in nitrogen.

(*b*) *Results.*

The curve in fig. 5 shows the results of one of the first runs on oxygen. The *m*/*e* scale is the one determined for nitrogen. Four definite peaks appear at *m*/*e* = 7·9, 16·4, 18·1 and 31·7, with suggestion of something at *m*/*e* = 28.

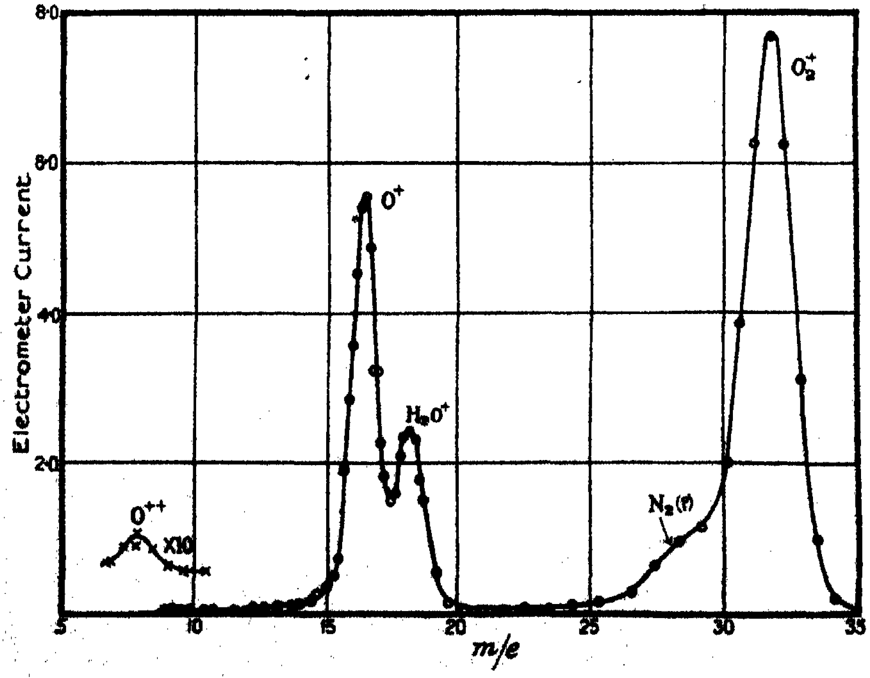

FIG. 5.—V_1 = 40; V_2 = 40 volts; H = 3020 Gauss; *i* = 500–300 microamps; *p* = 0·0012 → 0·0050 mm.

The different ions to which these are attributed are shown in the figure. Incidentally, it is of interest to notice the separation of the H_2O^+ peak from the O^+ peak and the suggestion of N_2^+ at 28, giving an idea of the degree of resolution obtained. In later runs these peaks were much reduced or entirely eliminated. The relative intensities of O_2^+, O^+ and O^{++} are typical and are similar to those found in nitrogen. In oxygen, however, the O^{++} was weaker and very troublesome to observe. The way the three intensities vary with V_1 is shown in fig. 6.

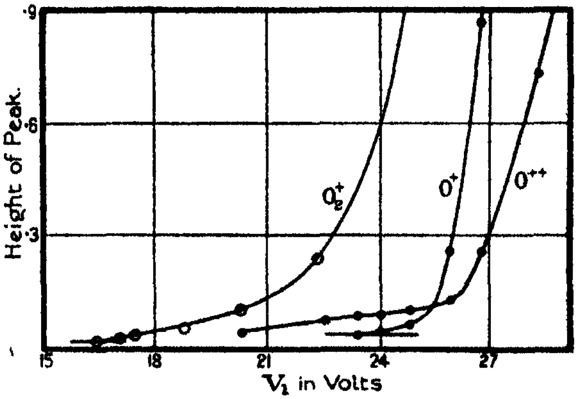

Fig. 6.—Series 5.

Before considering these curves it should be pointed out that the zero lines for O_2^+ and O^+ which appear to be drawn arbitrarily are actually determined by points off the peaks in individual runs.

The critical potentials $V_{O_2^+}$ and V_{O^+} are fairly definite, 15·6 and 24·3, as determined from the curve in fig. 6, and from consideration of the individual runs. But though the O^{++} evidently persists somewhat below the O^+ it is difficult to fix its point of disappearance exactly. On this account no values of $V_{O^{++}}$ are given in Table II, but this point will be discussed later. The assembled results for $V_{O_2^+}$ and V_{O^+} are shown in the following table.

As the last five series were taken with the same filament and approximately the same thermionic current, the correction to be applied to the observed voltages should be the same. In view of this, and the fact that Mackay's* recent work has thrown some doubt on the value of the ionizing potential, it was thought worth while to calculate the mean values. The correction for potential drop across the filament and initial velocity was of the order of

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* C. A. Mackay, 'Phys. Rev.,' vol. 21, p. 717 (1923).

Table II.—Results in Oxygen.

Series.	Fil.	H	i	p 10^{-2} mm.	Observed Potentials with Weights.		
					$V_{O_2^+}$	V_{O^+}	$V_{O^+} - V_{O_2^+}$
1	IV	3010	300–250	$0 \cdot 12 \rightarrow 0 \cdot 50$	18·3	25	—
2	V	3010	300–250	$0 \cdot 10 \rightarrow 0 \cdot 43$	17·3	26	7·7
3	V	2475	800–400	$0 \cdot 11 \rightarrow 0 \cdot 62$	—	24·5	—
4	VI	3010	500–200	$0 \cdot 08 \rightarrow 0 \cdot 31$	17·0 (2)	24·5 (3)	7·5 (6)
5	VI	3010	470–170	$0 \cdot 05 \rightarrow 0 \cdot 24$	15·6 (2)	24·3 (3)	8·7 (9)
6	VI	3010	400–300	$0 \cdot 09 \rightarrow 0 \cdot 45$	16·8 (5)	23·8 (3)	7·0 (15)
7	VI	3010	500–400	$0 \cdot 06 \rightarrow 0 \cdot 28$	—	24·3 (3)	—
8	VI	3010	500–300	$0 \cdot 06 \rightarrow 0 \cdot 28$	16·2 (4)	23·8 (4)	7·6 (16)
Weighted mean of last five series					16·46 ±0·59	24·12 ±0·1	7·53 ±0·2

NOTE.—In series 3 and 8 the current through the compensating magnet was shut off.

minus one volt. This gives about 15·5 as the true value, in agreement with the results of Foote and Mohler rather than Mackay.

Four series gave results for $V_{O^{++}}$ varying between 1·1 and 0·1 volts lower than V_{O^+} so that probably $V_{O^+} - V_{O^{++}}$ is about half a volt. One series, No. 3, was taken at a smaller magnetic field so that the V_3's required for O^+ and O^{++} were about the same as for O_2^+ and O^+ in the other runs, but no change was observed in the results.

Thus, if we assume $V_{O_2^+} = 15 \cdot 5$, we have $V_{O^{++}} = 22 \cdot 5$ and $V_{O^+} = 23 \cdot 0$. These are the voltages at which the different ions are first detectable, but before discussing their theoretical significance we will consider the changes in relative intensities as V_1 is increased.

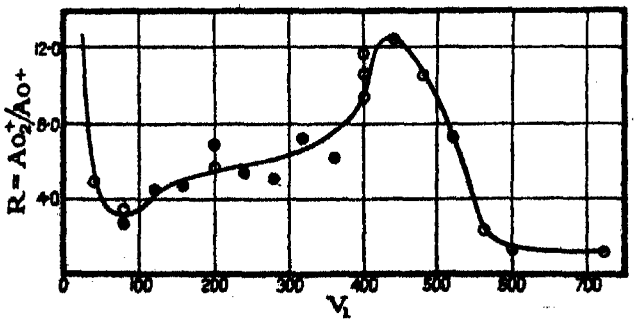

FIG. 7.

The curve in fig. 7 shows the variation in R, the ratio of the area of the O_2^+ peak to that of the O^+ peak as V_1 is increased. The points represent two series of runs taken on successive days. Though presented in a slightly different way, the results are similar to those in nitrogen. The relative value of O_2^+ diminishes up to 80 or 100 volts, and then rises gradually until about 450 when a sharp drop occurs. This drop is accompanied by a change in the character of the O_2^+ peak, which becomes not only smaller but broader and more diffuse, indicating that much of it is due to secondary effects. Another group of runs showed this change taking place more gradually and about a 100 volts higher. In these runs the compensating field had been zero, but the runs shown in fig. 7 were taken with the compensating field on. Further experiments showed that the relative intensities and character of the peaks at voltages from 400–600 were completely altered by turning the compensating field on or off. Time was lacking for a complete investigation of this point.

(c) *Discussion of Results.*

The most obvious result of the experiments on oxygen is the similarity of its behaviour to that of nitrogen. The first ionizing potential again corresponds to the production of a molecular ion, and again we have the peculiar result of doubly charged atomic ions appearing at a lower voltage than the singly charged, although this effect is much less marked in oxygen. For purposes of comparison the critical potentials are given in Table III.

Table III.

Type of Ion.	Critical Potential.	
	Nitrogen.	Oxygen.
Singly charged molecule	16·9	15·5
Doubly charged atom	24·1	22·5
Singly charged atom	27·7	23·0

Thus, we might expect a series of excitation potentials for oxygen such as Brandt found for nitrogen and, similarly, should try to connect the critical potential at 15·5 volts with the band spectrum. Foote and Mohler found a single excitation potential at 7·9 volts, but as they also only detected a single potential for nitrogen their experiments cannot be regarded as conclusive. There is not enough evidence available on the band spectrum to make any correlation possible.

In discussing the results on nitrogen, the writer suggested the probable transitions at the different critical potentials and gave corresponding energy equations involving the heat of dissociation, ionization potentials of the molecule and atom, and electron affinity of the atom. This type of reasoning has been quite extensively[*] used, and in the case of the hydrogen halides has predicted the ionising potentials within the limits of error. The experiments of Prof. Compton and the writer[†] suggest that it may also apply for the ionization of molecular iodine. However, the strongest justification for its application to a non-polar compound like nitrogen was its supposed validity for hydrogen. But the experiments described in Part I show definitely that it does not apply to hydrogen, and, therefore, the advisability of interpreting the results on oxygen by such a line of reasoning seems doubtful. Suffice it to say that a set of equations exactly analogous to those for nitrogen can be formulated, but that they require an ionizing potential for the oxygen atom about 5 volts lower than that computed from Hopfield's spectroscopic data.[‡] At present, it seems best to present the results merely as experimental observations, hoping that further investigation will make their theoretical significance clear.

As to the results at high voltage, it still seems probable that there is a critical point where the impacting electron penetrates more deeply into the molecule and the probability of dissociation rises sharply. Further, this critical point is higher for oxygen than for nitrogen, as is to be expected from its higher atomic number. Its exact value, however, is made doubtful by the marked effect produced by the variation of the magnetic field in the ionization tube. This effect may be explained in two ways. It may have been due to variation of the paths of the impacting electrons, so that the ions getting through the first slit were produced by electrons of different effective speeds with different magnetic fields. This seems improbable as the value of the compensating field had no effect on the critical potentials at low voltages (Table II, series 8). On the other hand, the magnetic field probably has a direct effect on the stability of the excited molecule, as suggested by Franck and Grotrian[§] and in this way caused the marked change observed in the relative proportions of the ions. This point suggests an interesting field for investigation.

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[*] Foote and Mohler, 'The Origin of Spectra,' Chap. VIII (1922).

[†] Smyth and Compton, 'Phys. Rev.,' vol. 16, pp. 501–513 (1920).

[‡] J. J. Hopfield, 'Nature,' vol. 112, p. 437 (1923).

[§] Franck and Grotrian. 'Zeits. für Phys.,' vol. 6, pp. 35–39 (1921).

GENERAL SUMMARY.

1. Using a method previously described, it is found that ionization in hydrogen at about 16·5 volts is not accompanied by dissociation as has been generally supposed.

2. Atomic hydrogen ions are first produced at a point 4·25 ± 0·06 volts higher than that at which molecular ions first appear.

3. The proportion of atomic ions remains very small up to 720 volts, the highest value used.

4. If sufficiently high pressure is used atomic ions predominate over molecular ions and appear at approximately the same voltage. This is interpreted as a secondary effect due to collisions of the ionized molecules with other molecules resulting in dissociation.

5. Results are obtained in oxygen similar to those previously found in nitrogen. Molecular ions are produced at about 15·5 volts, doubly and singly charged atomic ions at about 7 and at 7·5 ± 0·2 volts higher, respectively.

6. It is pointed out that these results can be interpreted by thermochemical equations such as were used for nitrogen, but that the results on hydrogen make the value of this procedure doubtful.

7. A sharp increase in the proportion of atomic ions was found in the neighbourhood of 500 volts, but this result was greatly affected by the value of the magnetic field in the ionization tube.

As this paper marks the end of the writer's connection with the Cavendish Laboratory, he wishes particularly to express his appreciation of Sir Ernest Rutherford's unceasing kindness and stimulating interest, which have contributed so largely to the pleasure and profit of two years at Cambridge. The writer's thanks are also due to the National Research Council for their continued support.

Summary of the Results obtained from Experiments made during the Years' 1918 to 1923 of the Effects of Temperature on the Properties of Metals.

By A. Mallock, F.R.S.

(Received December 4, 1923.)

During the period included between the years 1918 and the present time, I have carried out a considerable series of experiments on the effects which variations of temperature produce on the elasticity and other constants of various metals. Some of these are described in these 'Proceedings' (vol. 95, A, 1919; and vol. 97, A, 1920), also in a lecture given at the Royal Institution on May 27, 1921, and again in these 'Proceedings' (vol. 103, A, 1923).

In the present note I propose to give a summary of the results at present obtained. The method and apparatus used have been already described in the above-mentioned papers and need not therefore be here referred to.

In the earlier experiments the property examined was the variation with temperature of Young's Modulus, and it was found that the rate of variation depended chiefly on the melting point of the metal, and that the more fusible the metal, the greater was the change which the Modulus underwent for a given change of temperature. In this series the temperature ranged from 100° to −176° C. Considering that Young's Modulus is complex, involving both volume elasticity and rigidity, further experiments were made on the rigidity alone of the same metals.

Here the results agreed with those of the first series in showing that the variation of rigidity, as well as of Young's Modulus, depended chiefly on the melting points, and that in general the ratio of the absolute melting point to the melting point centigrade is somewhat less than the elastic constant at absolute zero to its value at 0 centigrade.

With regard to substances other than metals, I have not sufficient experience to warrant any sort of general statement, but in many instances the variations of rigidity are very large, and appear to depend rather on the molecular than on the chemical properties of the material. Indiarubber, for example, is more than a thousand times more rigid at the temperature of liquid air than at the freezing point of water, while with ebonite, which is only a more highly vulcanised rubber, the rigidities at these temperatures only vary in the ratio of 1·5 to 1.

The work done during the present year has been in connection with the properties of iron and steel. As is well known both iron and steel change into an allotropic form when the temperature is raised above a certain point (about 800° C. for iron and less for steel), and it would not be surprising if with the change of state, a discontinuous change also occurred in the elasticity and other co-efficients.

The experiments deal with the co-efficients of rigidity, thermal expansion, viscosity and specific heats, through a range of temperature extending from 14° to 1000° C. The rigidity co-efficient, or rather its variation, was determined by observing the torsional periods of a wire at different temperatures, the latter being measured by a platinum-rhodium thermo-couple placed within the heating coil. The rate at which the oscillations died out gave the required information as to viscosity. Thermal expansion was measured in two ways :—

(*a*) By an automatic record of the variations of the length of the wire in the heating coil, both in heating and cooling : and

(*b*) By a similar record of the variation of length of the wire heated by the passage through it of an electric current and then allowed to cool by radiation. In this case the wire was enclosed in a wide tube filled with nitrogen.

The experiments under the conditions of (*a*) give a true measure of the thermal expansion, for in this case the temperature of the wire closely conforms with that of the heating coil. Under the conditions of (*b*) however, where the only source of heat is that contained in the wire itself, the phenomenon of recalescence is observable, accompanied by expansion and the evolutions of heat as the metal passes from the high- to the low-temperature form, and in the absence of such experiments as those of (*a*), it would be open to question whether the re-extension was wholly due to the rise of temperature or in part to some molecular re-arrangement.

When two heated bodies of the same dimensions and the same quality of surface are allowed to cool in similar conditions, the rate of cooling of each is inversely proportioned to the specific heat, and as there is no reason (so far as I know) to suppose that the nature of the surface of iron or steel differs in the high- and low-temperature state, the rates of cooling as recorded in the (*b*) experiments give a measure of the ratio of the specific heats of the material on either side of the critical temperature.

The only property of iron and steel (leaving out of consideration magnetic and electrical constants) which undergoes a discontinuous change at this temperature is, apparently, the specific heat, and this change is not noticed in any of the many papers on the subject of recalescence which, by the kindness of Sir William Barrett, F.R.S., I have been able to examine.

A source of delay in my own work has been the difficulty of procuring pure iron and pure carbon steel. Pure iron is not commercially obtainable, and steels generally contain other substances besides carbon. It was not till late in the present year that, by the help of Sir Robert Hadfield, F.R.S., I was supplied with four samples, one of which was nearly pure iron and the others steel with carbon contents of 0·08, 0·51 and 0·8 respectively.

Figs. 1, 2, 3 and 4 are records of the variation of extension made with these samples by method (*b*).—The complete analysis and the approximate temperature scale has been added to each record.

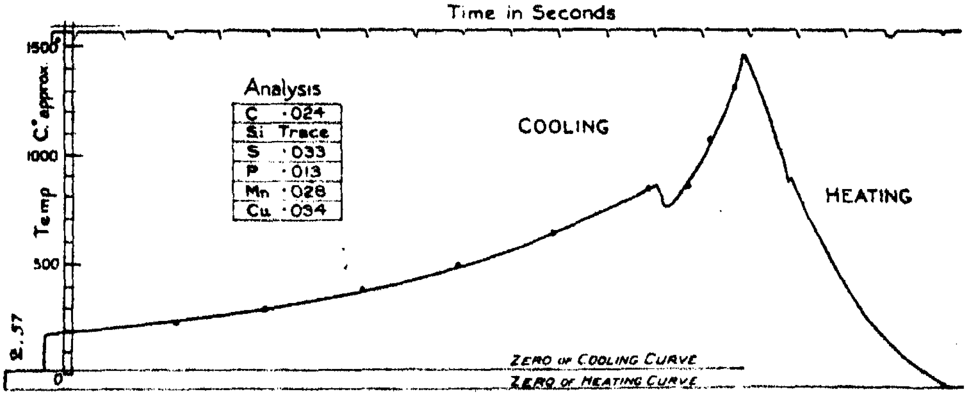

FIG. 1.—" Armco " Iron.

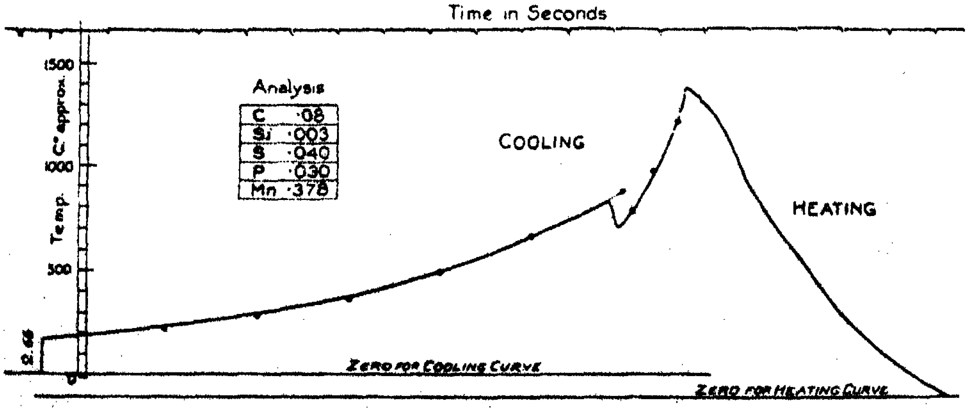

FIG. 2.—Mild Steel

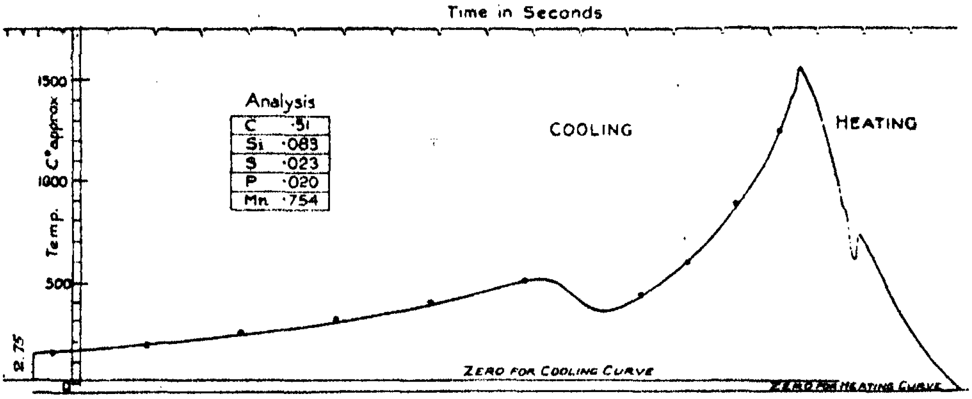

FIG. 3.—Siemens-Martin Steel.

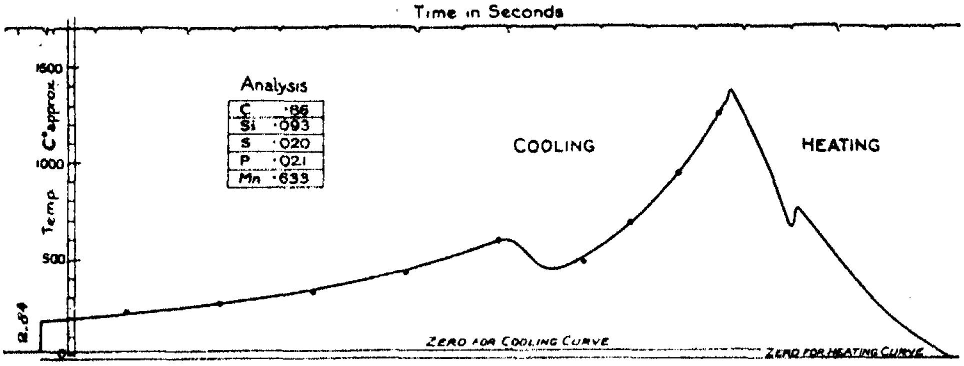

FIG. 4.—Siemens-Martin Steel.

These records show very clearly the differences in the rates of cooling between the high- and low-temperature states, and also that in the case of steel the carbon is the active cause of the reduction of the charted temperature.

In the course of time, I hope to be able to test really pure iron and a large variety of pure carbon steels, but meanwhile the results as far as the recent experiments are concerned may be summarized as follows :—

Thermal Expansion.

At low temperatures up to 200° C., the coefficient of expansion is the same both for iron and steel, and averages 0·00014 for centigrade degree.

As the temperature rises the coefficient diminishes.*

There is no discontinuous change at the critical temperature, and the variation appears to be independent of the change of state.

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* I omit the numerical value of the diminution until I have secured greater accuracy in the measurements of temperature.

The critical temperature for the metal of fig. 1 (nearly pure iron) is about 800° C. For the mild steel of fig. 2 it is 760° C.

Fig. 3 is for steel of 0·5 per cent. carbon, and here the critical temperature is 470° C.; while for the 0·8 per cent. carbon of fig. 4 the critical temperature is 510° C.

Specific Heat.

The ratio of the specific heats of the material in the high- and low-temperature states is inversely as the rates of cooling at the same temperature.

Assuming that the temperature θ at the time t after cooling begins is proportional to e^{-ct}, and that the variation of the length is proportional to θ—an assumption which though not strictly true is more nearly correct than the variation of the thermal expansion coefficient might seem to imply—the complete curve for cooling can be computed for both states (spots on the curves so computed are marked on the records in figs. 1 to 4) and the ratio of the specific heat is the ratio c_1/c_2 in the expressions e^{-c_1t} and e^{-c_2t}.

Thus it is found that for—

$$\text{Iron} \left\{\begin{array}{l}\text{Specific heat in low-temperature state}\\ \text{Specific heat in high-temperature state}\end{array}\right\} = 3\cdot25.$$

Mild steel .. .. = 3·32.
0·5 per cent. carbon steel .. .. = 3·15.
0·8 per cent. carbon steel .. .. = 3·50.

Having regard to the fact that the impurities such as Si, S, P, and Mn appear in different proportions in each of the steels, it is safe only to say that the specific heat ratio is somewhat greater than 3.

Rigidity and Viscosity.

The elastic rigidity of iron and steel is identical at the same temperature, and diminishes slowly from ordinary temperatures to that of a low red heat. The limits of elasticity of the two are, however, widely different, being very small for iron and increasing with the carbon content of the steel.

At a temperature of about (but somewhat below) 800° C., the rigidity and the elastic limits begin to diminish rapidly, and the viscosity effects are very evident, as shown by the rate of extinction of the torsional vibrations whose period gives a measure of the rigidity. The changes in rigidity and viscosity are not coincident with the change of state, and this is particularly noticeable in the steels with high carbon content.

In figs. 5 and 6 the curves show diagrammatically in terms of temperature the various quantities considered in this note.

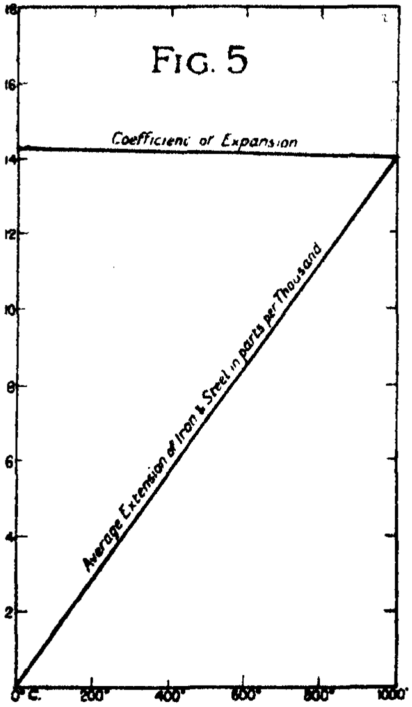


FIG. 5

Expansion Diagram.

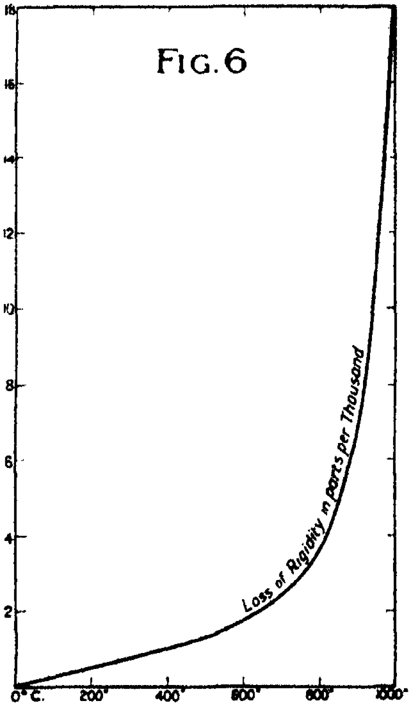


FIG. 6

Rigidity-loss Diagram.

I wish to add my best thanks to the Davy Faraday Laboratory, where these experiments have been carried out, and to Sir Robert Hadfield for the facilities and help given by them in connection with the investigation.

Note to Figs. 1–4.

These diagrams are reproductions of automatic records of variation of length, during heating and cooling, of wires 10 miles long and 0·02 inch diameter. (Ordinates 7·5 times actual size.)

The spots on the curves are values computed on the assumption that the variation of length, after cooling begins, is proportional to e^{-ct}, where t is time elapsed, and c a constant inversely proportional to specific heat.

Catalytic and Induced Reactions.—Part I. *Catalytic and Induced Oxidation in the Presence of Salts of Cerium.*

By Arthur Kenneth Goard (Coutts-Trotter Student, Trinity College, Cambridge), and Eric Keightley Rideal.

(Communicated by Prof. T. M. Lowry, F.R.S.—Received December 6, 1923.)

§ 1. Historical.

Work upon the phenomena of induced oxidation dates from the researches of Schönbein (1), who showed that during the autoxidation of many substances —*e.g.*, turpentine and benzaldehyde—for every molecule of oxygen consumed by the primary substance undergoing oxidation, another molecule of oxygen was simultaneously transformed into a more active state; this active oxygen could then react secondarily with more oxygen, forming ozone; with water, forming hydrogen peroxide, or with certain other substances—*e.g.*, indigo blue—effecting oxidations which could not be accomplished by ordinary atmospheric oxygen. This activation of oxygen Schönbein termed "ozonisation"; as the result of the observation that ozonised turpentine reduces lead dioxide to the monoxide, he was led to the supposition that active oxygen exists in two forms of opposite sign, which he termed ozone and antozone. He thereby adopted the conception of polarity previously introduced by Brodie (2), though the latter did not support Schönbein in his division of the peroxides of the alkalies and of the heavy metals into antozonides and ozonides respectively.

R. Clausius (3) stated that ozone and antozone could be regarded as oppositely charged oxygen ions, a view adopted by van't Hoff (4), who suggested that the equilibrium

$$O_2 \rightleftarrows O^+ + O^-$$

already exists in atmospheric oxygen, since he had observed that when phosphorus undergoes autoxidation in the presence of indigo, a continual supply of fresh indigo was necessary in order to maintain the reaction velocity at a reasonable figure; this, he considered, supported the above hypothesis, since accumulation of ozonic oxygen (removed by excess of indigo) would diminish the active mass of the antozone oxidising the phosphorus.

Nevertheless, attempts to prove the existence of ozonised oxygen have yielded results, which are at best inconclusive; and the majority of later experiments have tended to bring the conception of the intermediate compound, introduced by A. Bach (5), C. Engler (6), and others, into greater and greater prominence.

According to these workers, activation of the oxygen takes place through the formation of a peroxide of the primary substance (the autoxidiser, or "inductor"), which then, in the presence of another oxidisable substance (the "acceptor"), transfers a portion of its acquired oxygen to the acceptor, becoming itself a normal oxide, according to the general scheme :—

$$\underset{\text{(inductor)}}{A} + O_2 \longrightarrow AO_2 \qquad (1)$$

$$AO_2 + \underset{\text{(acceptor)}}{B} \longrightarrow AO + BO. \qquad (2)$$

This view was supported by the experimental discovery of many peroxides of substances observed to act as inductors, including that of benzaldehyde, isolated in 1900 by Baeyer and Villiger (7). Two important examples, for the explanation of which the peroxide theory has been invoked, are (*a*) induced oxidation in the presence of iron salts, investigated by Manchot, (*b*) the induced oxidation of arsenites in the presence of salts of cerium. The former will be discussed in Part II of this paper ; the latter, which has been studied chiefly by A. Job, Engler and Wild, and E. Baur, will be briefly considered here.

Job (8) showed that cerous salts were dissolved in concentrated potassium carbonate solution, giving a colourless liquid which on exposure to air turned dark red, owing to the formation of a complex carbonate, which he was able to isolate, in which cerium exists in the sexavalent condition. Ammonium ceric nitrate, on the other hand, gave under similar circumstances a yellow solution which remained unchanged towards air. It follows necessarily from these observations that on oxidation the cerous compound attains the perceric state directly, without passing through the intermediate ceric stage.

This cerous solution when acted upon by atmospheric oxygen in the presence of excess of potassium arsenite, assumes the quadrivalent ceric state, with fixation of oxygen upon the arsenite, after which the process stops, save for the very slow spontaneous oxidation of potassium arsenite. Some discrepancy appears in the results of different investigators as to the proportion of oxygen activated by the cerium. Baur (9) obtained an activation proportion of two molecules of oxygen fixed upon the arsenite to one molecule fixed upon the cerium, by means of experiments upon the absorption of oxygen by the mixture ; Engler and Wild (10) obtained a proportion of 1 : 1. Baur, however, repeated his experiments (11) and confirmed his earlier results. Engler's results he attributed to the acceptor action of the cerous salt itself. By using smaller quantities of arsenite, Job was further able to show that the cerous solution on shaking with air exhibited momentarily a reddish colour before changing to the yellow ceric state.

The oxidation of cerous salts by means of atmospheric oxygen thus induces the oxidation of sodium arsenite, and when all the cerous salt has been converted into the ceric state the reaction ceases. Cerium salts, however, can be made to exert a catalytic effect on the oxidation of sodium arsenite, or a very small quantity of a cerous salt can, under suitable conditions, effect the atmospheric oxidation of an indefinite quantity of sodium arsenite. Job found that the simple addition of glucose to the solution undergoing oxidation was able to effect the conversion of the reaction from one of the coupled or induced type to one of the purely catalytic variety. If excess of glucose were added to the solution, the fixation of oxygen, instead of ceasing at the stage mentioned above, continued indefinitely, since the reducing action of the glucose, though slower than that of potassium arsenite, was more profound, the ceric solution being completely decolorised and reduced to the cerous state, in which cerium is once more capable of fixing atmospheric oxygen.

Cerous salts, dissolved in concentrated potassium carbonate solution, therefore provide an example of induced oxidation with respect to the acceptor potassium arsenite, and an example of catalytic oxidation with respect to glucose, reaction proceeding by the intermediate formation of a perceric salt.

The conditions under which a coupled or induced reaction is capable of being converted into a continued or catalytic action, and *vice versa*, was considered of sufficient interest to warrant a closer investigation.

§ 2. THEORETICAL.

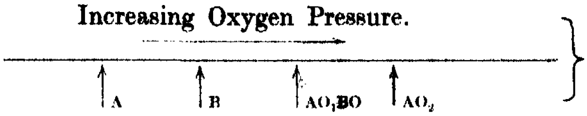
It is well known that the potential of an unalterable electrode, when immersed in a solution of an oxidation-reduction mixture, may be expressed, theoretically at least, as a function of the free energy of the given oxidation-reduction process. In the sequel the term "oxygen pressure" will be adopted to denote the oxidising ability of the solutions of substances examined, as apparent from potential measurements. This term is employed merely for convenience, a direct physical significance is not implied.

Suppose an inductor, A, and an acceptor, B, react according to the following equations :—

$$\underset{\text{(atmospheric)}}{A + O_2} \longrightarrow AO_2 \tag{1}$$

$$AO_2 + B \longrightarrow AO + BO. \tag{2}$$

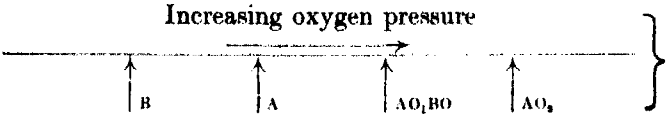
If now the oxygen pressures of the compounds involved follow the order :—



Scheme I.
Coupled Reaction.

induced oxidation might be expected. Under these circumstances, oxygen, acting upon the inductor A, raises the oxygen pressure of the solution to a high value, denoted by the potential of AO_2, so that the acceptor B is oxidised, with the reduction of the peroxide of A to the oxide AO, and a lowering of the oxygen pressure to some intermediate value at which AO and BO exist together in equilibrium. Since the oxygen pressure of A lies below that of B, the reaction will stop at this point, for B will be unable to reduce AO to the initial state, A, at which fresh peroxide could be formed.

If, on the other hand, the potentials observe the order



Scheme II.
Catalytic Reaction.

the reaction should be catalytic, since the peroxide AO_2 will be reduced by B to the initial state, A, provided a sufficient excess of B be present ; A will thus be able to " fix " atmospheric oxygen to an indefinite extent.

The above simple statement needs a little modification. The potential of a pure substance is theoretically infinite, the curve connecting the potential with the percentage composition of a mixture such as X and XO (*e.g.*, Fe^2 and Fe^3), being of the form

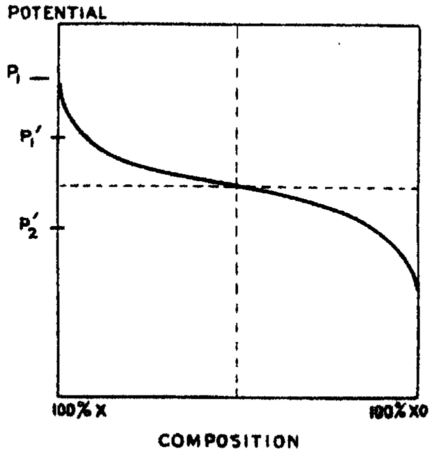


Fig. 1.

The values given above for the oxygen pressures of A, B, AO_2, etc., should therefore be interpreted as follows :—

Oxygen pressure of AO_2 = the observed potential of that mixture of A and AO_2 which is obtained when atmospheric oxygen is passed through a solution of A until equilibrium is reached.

Oxygen pressure of BO = a potential corresponding to that mixture of B and BO which is obtained when the coupled system has finally reached equilibrium. For the majority of mixtures this potential will lie between the comparatively narrow limits P'_1, P'_2 in the above diagram.

The oxygen pressure of AO should be similarly interpreted.

Oxygen pressure of A and B = potentials corresponding roughly to P_1 in the above diagram. This potential will be that obtained in practice with ordinarily pure solutions of A and B, and represents a pressure below which A and B can only exist in a state of virtually complete reduction.

For the sake of brevity, this potential will hereafter be referred to as the "limiting or P_1 value" of the substance in question.

§ 3. EXPERIMENTAL.

The system chosen for the investigation of the above oxygen pressure relations was that of potassium arsenite dissolved in a concentrated solution of potassium carbonate in the presence of cerous salts. This case has been discussed in § 1 of this paper ; here the cerous salt corresponds to the A, the perceric salt obtained by the action of atmospheric oxygen to the AO_2, potassium arsenite to the B, and the arsenite-arsenate mixture in equilibrium with ceric salt to the AO BO of the preceding scheme.

Apparatus Employed.

Standard Electrode.—A saturated calomel electrode of the Sand type, possessing an E.M.F. of 0·2464 volts at 25° C. against the normal hydrogen electrode.

Potentiometer.—An open wire potentiometer working upon a Null-point system, combined with a sensitive dead-beat galvanometer and a Weston cell. This instrument was capable of reading to 0·1 millivolt ; the internal resistance of the cell system, however, made direct reading to less than 0·5 millivolt impracticable.

Electrodes.—About 2 inches of polished platinum wire, fused by means of blue enamel into Duro glass tubes.

Junction Liquids.—The cell was connected by means of a tube containing 3·5 N potassium chloride solution to a small vessel containing 7 N potassium carbonate solution (*i.e.*, 3·5 mols. per litre); this in turn was connected to the solutions under measurement.

The *Solutions* of arsenite, cerous carbonate, etc., all contained 2·49 mols. of potassium carbonate per litre.

The apparatus was immersed in a thermostat kept at 25° C.

(*a*) *The Potential of Potassium Arsenate.—Arsenite Mixtures.*

A difficulty incurred at the outset of these experiments was the irreversible behaviour of the platinum electrode with respect to these mixtures, by virtue of which it was at first impossible to obtain a reproducible potential. The causes underlying this behaviour have been discussed elsewhere by the present authors (12), and the phenomenon was shown to be due to the slow but progressive denudation of oxygen contained in the electrode, probably as oxide, by the arsenite, resulting in a drift of the potential towards more oxidising values. Reproducible initial potentials were obtained if the electrode previous to immersion in the arsenite mixture were placed, after boiling with hydrochloric acid and ignition in a methyl alcohol flame, in a solution containing 10 c.c. of decinormal potassium permanganate solution and 90 c.c. of borate buffer solution of P_H9, and kept in this mixture for $\frac{1}{2}$–$\frac{3}{4}$ hour, with vigorous stirring. If the electrode so treated were then washed and inserted in the arsenate-arsenite mixture, the potential was observed to rise rapidly, towards reducing values, until a definite maximum was reached, after which the potential fell once more towards oxidising values—the solution having been gently agitated immediately after insertion of the electrode and then allowed to rest.

This maximum potential was reproducible to a considerable degree of accuracy. An electrode which had been merely boiled with hydrochloric acid and ignited in a methyl alcohol flame gave initial potentials varying irregularly within a range of 0·03 volt or more; with a "controlled" electrode it was possible, after a comparatively small number of determinations, to determine the potential of a given mixture to within one or two millivolts.

The following results were obtained with solutions containing dissolved arsenious and arsenic oxides, together equivalent to 0·0144 mols. per litre:—

Molecular percentage		Potential (volts)	Mean values (volts)	
As^{III}	As^{V}	Observed (E obs.)	(E obs.)	Potential against the normal hydrogen electrode (E_H)
97·5	2·5	0·210 0·204 0·207 0·209	0·2075	+ 0·0389
90·0	10·0	0·195 0·198 0·193 0·194	0·1950	+ 0·0514
75·0	25·0	0·191 0·190 0·191 0·196 0·192	0·1920	+ 0·0544
50·0	50·0	0·1915 0·184 0·194 0·189 0·186 0·197 0·180 0·182 0·195	0·1887	+ 0·0577
25·0	75·0	0·1795 0·186 0·1855 0·190 0·1845 0·1835 0·176	0·1836	+ 0·0628
10·0	90·0	0·169 0·170 0·169	0·1693	+ 0·0771
2·5	97·5	0·155 0·1495 0·157 0·153	0·1536	+ 0·0928

It will be apparent from the curve on which these results are plotted that the limiting or P_1 value of potassium arsenite under these conditions lies at about 0·230 volts, the calomel electrode being the positive pole of the cell, or $E_H = + 0{\cdot}016$ volts.*

Two reservations must be made: (1) The liquid-liquid junction potentials have not been ascertained; (2) the results obtained with the controlled electrode cannot be taken as reversible potentials.

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* A positive sign is given to E_H if in combination with a normal hydrogen electrode, the platinum immersed in the solution under consideration would act as the positive pole of the cell.

As regards (1), since the experiments described are concerned merely with relative potentials this constant factor does not enter into consideration; (2) will be considered later.

(b) *The Potential of Potassium Cerous Carbonate.*

The cerous salt employed was a pure specimen of cerous sulphate, $Ce_2(SO_4)_3$, $5H_2O$. This salt dissolved slowly in distilled water, yielding a colourless stable solution; on addition of this to concentrated potassium carbonate solution, a colourless precipitate of cerous carbonate was at first thrown down, which immediately dissolved, giving a clear solution which rapidly darkened in colour owing to formation of perceric salt.

In order to determine the potential of "pure" cerous carbonate solution it was obviously necessary to eliminate atmospheric oxygen from the solution as completely as possible. Measured quantities of potassium carbonate solution, and of cerous sulphate solution, were therefore boiled and cooled separately in an atmosphere of nitrogen freed from oxygen by passage over copper turnings heated in an electric furnace, and the latter solution added to the former without contact with air. Since it was found unnecessary to treat the platinum electrode in any special manner, the cerous solution giving definite and stationary potentials, the electrode was allowed to remain in contact with the potassium carbonate solution before addition of the cerous sulphate.

The latter was added through a dropping funnel without contact with air. The mixing of the solutions was effected by the passage of nitrogen; a clear colourless solution was thus obtained, of the composition 2·49 mols. K_2CO_3, 0·00218 mols. cerous salt, per litre.

As a result the following potentials were observed, which showed no drift among themselves :—

Expt.	E obs.	E_H (volts).
I	0·314	−0·0676
II	0·320	0·0736
III	0·316	0·0696
IV	0·3175	0·0711
V	0·316	0·0696
VI	0·329	0·0826
VII	0·322	0·0756
VIII	0·319	0·0726
Mean value	0·3190	−0·0726

The variation in the readings indicates that the traces of oxidation product in the solution were exceedingly minute, which was confirmed by the fact that the potential was very sensitive to the presence of oxygen. The passage of a regulated current of air through one of these solutions gave the following initial readings :—

Time (mins.).	E obs. (volts).	Time (mins.).	E obs. (volts).
0	0·319	10	0·242
1	0·280	20	0·219
2	0·271	29	0·2065
4	0·261	41	0·192
7	0·251	50	0·180

It will thus be seen that the limiting or P_t value of potassium cerous carbonate, in a solution of the above composition, may be taken at 0·320 volts [$E_H = -0\cdot074$ volts].

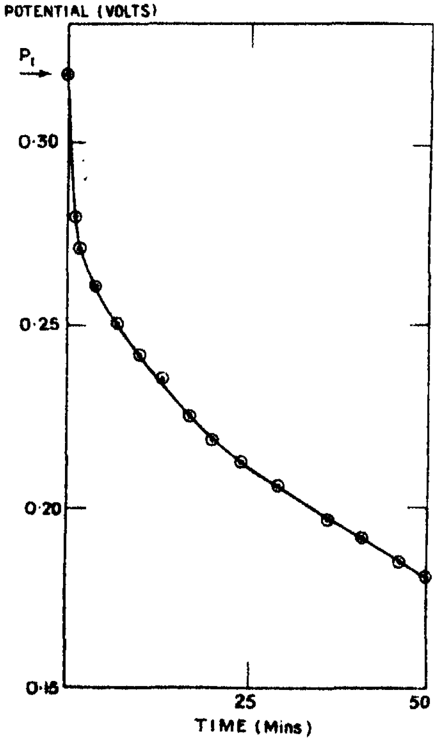


FIG. 2.

(c) *The Potential of Ceric Peroxide.*

Air, passed first through concentrated potash solution and then through a solution of potassium carbonate containing 2·49 mols. of K_2CO_3 per litre, was bubbled through solutions of cerous carbonate of the above composition for about 14 hours, the whole apparatus being kept at 25° C.

The resulting solutions, which were dark reddish-brown in colour, gave the following potentials :—

Expt.	E obs.	E_H (volts).
I	0·007	+0·2394
II	0·0045	0·2419
III	0·0058	0·2406
Mean value	0·0058	+0·2406

(d) *The Potential of Ceric Salt.—Arsenate-Arsenite Mixtures.*

Some experiments of type (*c*) were carried out in which dissolved arsenious oxide was present in the solution. Under these circumstances, the resulting solution, which was canary-yellow in colour, owing to the existence of the bulk of the cerium in the quadrivalent condition, gave definite and stable potentials with respect to the platinum electrode. The results obtained were as follows :—

A. Solution containing originally

2·49 mols. K_2CO_3 per litre,
0·00218 mols. cerous salt per litre,
0·0144 mols. As_2O_3 per litre.

Expt.	E obs. (volts).
I	0·138
II	0·137
III	0·138
IV	0·136
Mean value	0·1373 ; $E_H = +0·1091$ volts.

B. Similar solution, containing 0·00432 mols. As_2O_3 per litre.

Expt.	E obs. (volts).
I	0·136
II	0·134
III	0·136
IV	0·136

Mean value ...... 0·1354 ; E_H = + 0·1110 volts.

C. Similar solution, containing 0·00288 mols. As_2O_3 per litre.

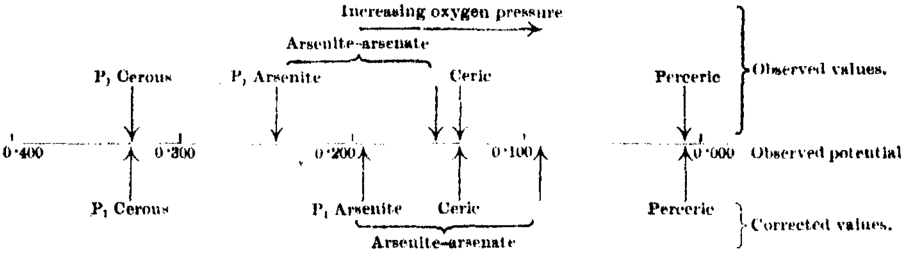
Expt.	E obs. (volts).
I	0·133
II	0·131
III	0·133
IV	0·132
V	0·132

Mean value ...... 0·1322 ; E_H = + 0·1142 volts.

A blank experiment, using the controlled electrode, showed that in the absence of cerous salt the spontaneous oxidation of the potassium arsenite during the passage of air was less than 2 per cent.

If the cerous atom activate two atoms of oxygen, the maximum oxidation of the arsenious oxide in the above experiments is (A) 15 per cent. ; (B) 50 per cent. ; (C) 75 per cent. Under these conditions it is improbable that oxidation actually proceeds as far as this ; assuming it to be so, however, these values will be found to lie on a curve approximately parallel to the arsenite-arsenate curve previously investigated, but lower than this curve by (A) 0·055, (B) 0·053, (C) 0·051 volts. Since the cerous-ceric system must be assumed to be in equilibrium with the arsenate-arsenite mixture, and since the former appears to act as a "depolarisation catalyst" with respect to the platinum electrode, it is probable that the difference of 0·053 volts represents the difference between the controlled electrode acting irreversibly in the arsenate-arsenite mixture, and the reversible electrode ; *i.e.*, that the values obtained with the controlled electrode should be lowered by 0·053 volts in order to represent the values which would have been obtained were the electrode capable of acting reversibly. In the sequel these "corrected" values will be given, as well as those observed ; it will be seen, however, that whether this argument be justifiable or not the immediately important point of the relative order of the potentials is not affected.

(*e*) In the following diagram these potentials are given in order of increasing oxygen pressure ; observed values are given above, corrected values below.



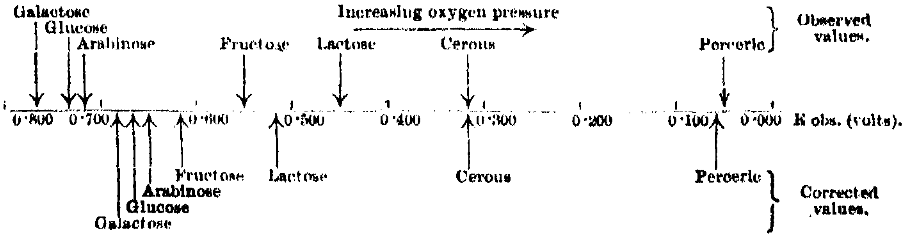
On comparison of this diagram with Scheme I of § 2 above it will be evident that the two orders are identical.

(*f*) *The Potential of the Reducing Sugars.*

It will be remembered that whereas the oxidation of potassium arsenite in the above system proceeds to a definite end-point, the oxidation of glucose through the agency of cerium salts is catalytic, proceeding indefinitely in the presence of sufficient excess of the former. We should therefore expect the potentials of glucose, cerous and perceric salts to observe the order given in Scheme II.

The potentials of glucose, lactose, arabinose, galactose, and fructose were consequently investigated. These substances behave *irreversibly* towards the platinum electrode, and if the latter be treated in the ordinary manner the potentials obtained show great and irregular variations. Satisfactory results can, however, be secured by means of the controlled electrode ; those obtained in the present investigation are shown in the Table below.

All the substances behaved exactly in the manner described by Job in the case of glucose. A comparison of their potentials shows that the order of Scheme II in §2 is obeyed.



	Mols. per litre.	E obs. (volts).	E_H (volts).
Glucose	0·397	0·710	
		0·715	
		0·720	
		0·730	
		0·723	
		0·720	
		0·715	
		0·719	
		0·729	
	Mean value	0·720	−0·474
Lactose	0·199	0·528	
		0·525	
		0·517	
		0·525	
	Mean value	0·524	−0·278
Arabinose	0·191	0·715	
		0·714	
	Mean value	0·7145	−0·468
Galactose	0·318	0·739	
		0·745	
		0·735	
		0·739	
	Mean value	0·7395	−0·493
Fructose	0·397	0·614	
		0·614	
	Mean value	0·614	−0·368

Summary.

An electrode of special type has been devised, whereby it is possible to effect the comparison of the potentials of certain substances which behave irreversibly towards the platinum electrode.

The action of cerous salts in effecting the induced oxidation of potassium arsenite, and the catalytic oxidation of five reducing sugars, have been investigated from the standpoint of oxidation potential. In the former case the potentials have been found to observe the order

Cerous salt (inductor)—arsenite (acceptor)—equilibrium mixture—perceric salt;

in the latter, the order

> Reducing sugar—cerous salt—perceric salt, as anticipated in the theoretical section of this paper.

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Catalytic and Induced Reactions. Part II.—Catalytic and Induced Oxidation in the Presence of Salts of Iron.

By Arthur Kenneth Goard (Coutts-Trotter Student, Trinity College, Cambridge) and Eric Keightley Rideal.

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The reactions comprised under this heading include many examples of physiological importance and others well known to chemists—*e.g.*, the separation of iodine from potassium iodide in the presence of ferrous salts and hydrogen peroxide, first discovered by Schönbein, the process being known consequently as "Schönbein's reaction"; and the oxidation of certain organic compounds in the presence of Fenton's reagent (ferrous sulphate and hydrogen peroxide).

Explanations of the observed phenomena have usually been based upon the hypothesis of an *intermediate compound of iron*; they have remained somewhat tentative, however, since direct evidence of the formation of such compounds has not been forthcoming. Manchot, who investigated Schönbein's reaction in a quantitative manner (1), came to the conclusion that hydrogen peroxide acted upon ferrous sulphate in neutral solution forming the peroxide

Fe_2O_5, since one equivalent of ferrous iron liberates two equivalents of iodine from potassium iodide, the latter being present in excess; allowing for the equivalent of oxygen necessary to transform ferrous iron into ferric, we obtain the total of three equivalents, or a formula of Fe_2O_5 for the intermediate compound. He reached a similar conclusion from the study of the action of chromic and permanganic acids upon ferrous sulphate in the presence of acceptors; he was nevertheless quite unsuccessful in any attempt to isolate the postulated peroxides, nor have subsequent investigators fared better. Manchot decided, however, that their formation must be supposed in order to explain his results; and some such hypothesis would appear to be necessary in order to account for the reactions investigated by Fenton and others (2).

Schönbein's reaction is complicated by the following factors: (*a*) hydrogen peroxide acts directly upon potassium iodide with liberation of iodine; (*b*) ferric salts have a slow but definite decomposing action upon hydrogen peroxide. Working in very dilute neutral solution, these factors can be sensibly eliminated; and the action of ferrous salts is then seen to resemble that of other inductors, a definite end point being obtained when nearly two equivalents of iodine have been liberated. The iodine liberation never reaches the theoretical value, owing to the secondary reaction

$$Fe_2O_5 + FeO \longrightarrow 3Fe_2O_3 \quad \text{(1)}$$

a reaction eliminated as far as possible by Manchot, by causing the ferrous solution to run slowly into the hydrogen peroxide, with vigorous stirring. Under ordinary conditions of titration reaction (1) occurs completely; Skrabal has shown (3) that salts of manganese exert a catalytic effect upon it; to the secondary process,

$$Fe_2O_5 + HCl \longrightarrow 4Fe_2O_3 + 2H_2O + Cl_2 \quad \text{(2)}$$

must, however, be ascribed the chlorine evolution observed when ferrous salts are titrated with permanganate in the presence of excess of hydrochloric acid (4).

Schönbein's reaction in acid solution follows a different course; the iodine separation is retarded, but continues indefinitely, no end point being reached. In other words, the salts of iron here act catalytically. Factor (*b*) also becomes relatively marked.

Manchot considered that he had obtained certain evidence of the formation of Fe_2O_5 in the absence of acceptors by adding ferrous sulphate to hydrogen peroxide and testing the product for ferrous iron. His results were criticised by Mummery (5), who regarded them as due to the reduction of the potassium ferricyanide used as indicator by hydrogen peroxide. The latter investigator studied the rate of decomposition of hydrogen peroxide by ferrous sulphate in neutral solution, adding 2½ mols. of the former to one of the latter, stopping the reaction at definite intervals of time by adding sulphuric acid and titrating the undecomposed peroxide with permanganate. Under these circumstances he found that rather more than 0·75 mol. of hydrogen peroxide were decomposed almost at once: a steady decomposition then set in, at first linear with the time, but falling off in rate when nearly all the hydrogen peroxide had been decomposed. He concluded from this that a small quantity of an intermediate compound was reversibly formed in solution, the rate of its decomposition having been measured in these experiments.

Ferric salts behaved somewhat similarly, save that no rapid initial decomposition was observed.

To summarise the preceding, it may be said that though the observed phenomena appear to demand the formation of the compound Fe_2O_5, the evidence of its existence is in all cases indirect, nor has it been possible to prove that the same compound is formed by the action of hydrogen peroxide upon ferrous salts in the absence of acceptors.

§2. *Experimental.*

The following experimental procedure was followed for the study of Schönbein's reaction from the standpoint of oxidation potential. The apparatus employed was similar to that described in Part I of this paper. With the substances investigated it was not necessary to employ the controlled electrode; the platinum wire electrodes were therefore merely boiled with hydrochloric acid, washed, and ignited in a methyl alcohol flame, and then immersed in the solutions under investigation, which were stirred vigorously in a beaker surrounded by melting ice.

The junction liquids employed were 3·5 N KCl and saturated K_2SO_4 solutions.

(*a*) *Potassium Iodide—Iodine Potentials.*

(i) *Neutral Solution.*

Solution employed: 40 c.c. neutral ($P_H = 7$) borax-boric acid buffer solution, made up according to Palitzsch.

10 c.c. N/50 KI, N/250 I (*i.e.*, 1/5 molar proportion of iodine).

Temperature 0° C.	E obs. (volts).	E_H (volts).*
	0·4135	+ 0·6625

* The room temperature during these experiments was 20° C., at which the potential of the saturated calomel electrode is 0·249 volts against the normal hydrogen electrode.

(ii) *Acid Solution.*

N/250 KI, N/1250 I, N/300 H_2SO_4.

Temperature 0° C.	E obs. (volts).	E_H (volts).
	0·4135	+ 0·6625

In accordance with the results of other investigators, the potential of the $KI-I_2$ mixture is thus seen to be independent of the P_H.

In the experiments of Manchot quoted above, the total amount of iodine liberated at the conclusion of each determination was approximately 1/5 grm. equivalent of iodine per grm. mol. of potassium iodide. The above experiments therefore represent the *upper* limit of the oxygen pressure of his potassium iodide-iodine mixture.

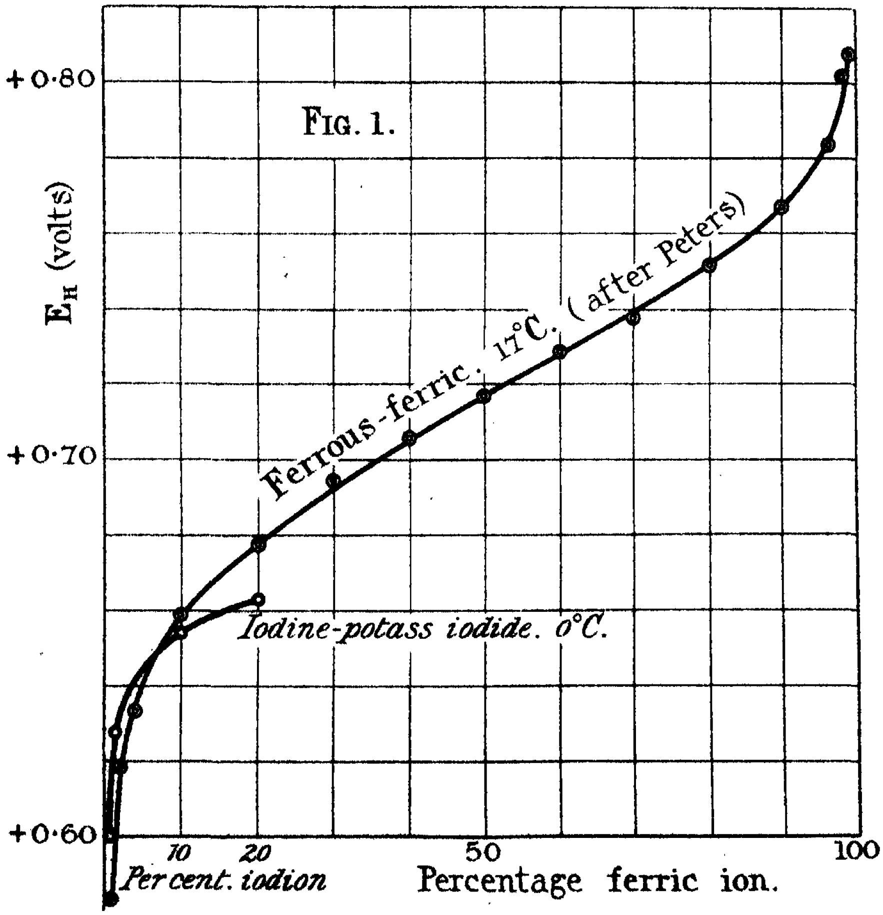


Fig. 1.

The following experiments were further carried out, using N/300 H_2SO_4, N/250 KI, at 0° C.

Molecular percentage of iodine.	$E_{(obs.)}$.	E_H (volts).
10	0·405	0·654
1·8	0·379	0·628
0·14	0·3515	0·6005

The limiting or P_1 value of potassium iodide can therefore be taken as about 0·325, or $E_H = 0·574$ volts (*see* fig. 1).

(*b*) *Ferrous-Ferric Potentials.*

In acid solution the potential of an unalterable electrode immersed in a mixture of ferrous and ferric ions is independent of the P_H. Towards neutrality, however, the oxygen pressure of ferrous salts falls rapidly with increasing P_H (decreasing acidity), assuming a very low value in alkaline solution.

The following measurement was carried out :—

Solution : 40 c.c. neutral buffer solution.
10 c.c. N/200 Ferrous ammonium sulphate solution.

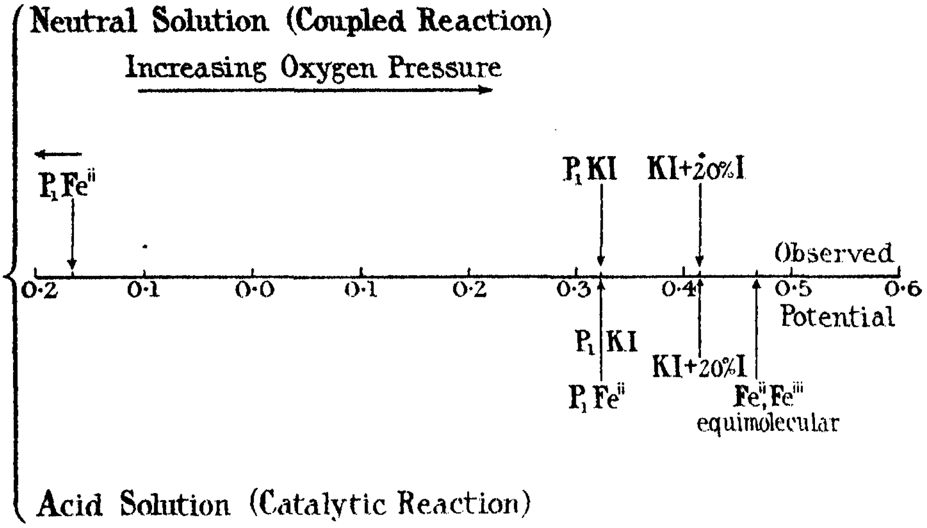
E obs.	E_H (volts).
0·166 (calomel $+^{ve}$)	0·083

This value, owing to atmospheric oxidation, is probably slightly higher than the true P_1 value of neutral ferrous solutions.

Acid Solution.—The potentials of ferrous ferric mixtures in N/10 hydrochloric acid at 17° C. have been determined by Peters, (6) and are shown reduced to the normal hydrogen electrode in the accompanying curve (fig. 1), the iodine-potassium iodide potentials being included for the sake of comparison.

The interesting point is thus brought out that in acid solution the limiting or P_1 values of potassium iodide and ferrous salt are practically identical. This is in full agreement with the well known analysis of ferric iron by Mohr's method ; virtually complete reduction of ferric iron to ferrous can only be effected in acid solution by the addition of a large excess of potassium iodide.

The results of the above experiments are tabulated below.



On comparison of these results with the scheme given in Part I of this paper, it will be evident that the general principles of coupled and catalytic reactions are obeyed. In neutral solution the oxygen pressure of the inductor (Fe^{II}) lies far below that of the acceptor (KI), so that the reaction is coupled; in acid solution the relatively high oxygen pressure of the inductor leads to its constant regeneration in presence of excess of the acceptor, so that reaction is catalytic.

(*c*) *The Action of Hydrogen Peroxide upon Ferrous Salts.*

The case of cerium investigated in Part I of this paper is exceptional, by virtue of the large percentage of peroxide compound existing in equilibrium with atmospheric oxygen, and the stability of the compound itself. The peroxide of iron, Fe_2O_5, is, on the other hand, so unstable that no direct evidence of its existence has hitherto been forthcoming. By means of potential measurements, however, it has been possible to demonstrate the existence of this oxide.

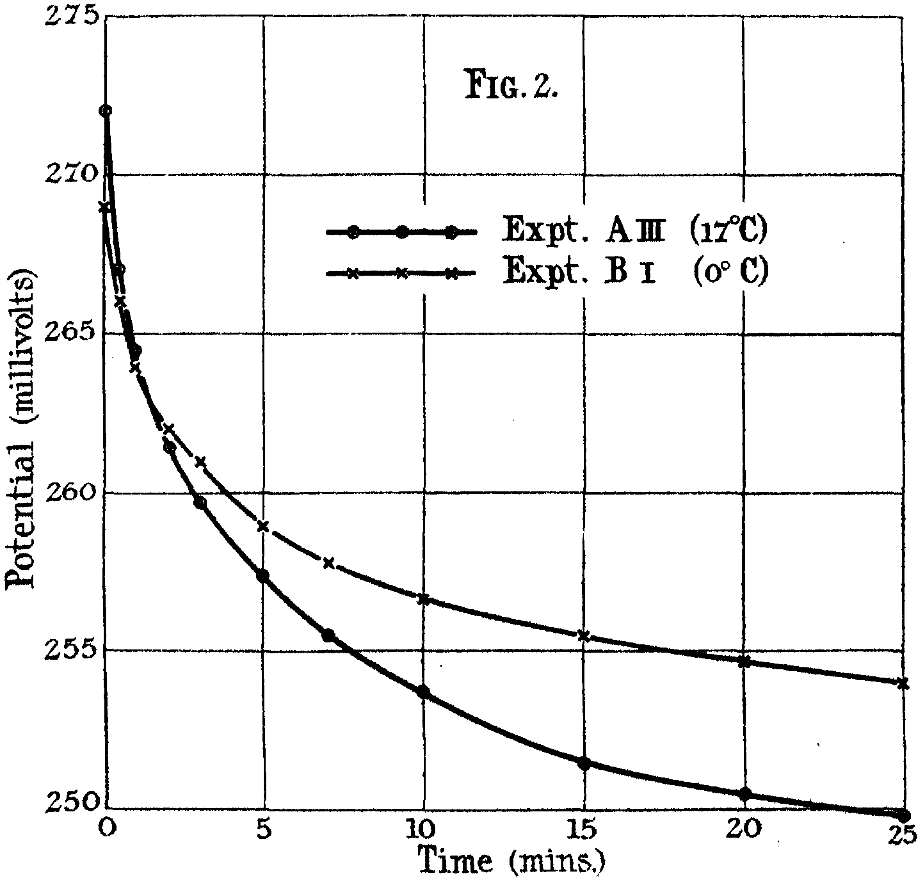
If a suitable quantity of ferrous ammonium sulphate solution be added to a neutral buffered solution of hydrogen peroxide, a small but definite rise of potential occurs, indicating the presence of a new oxidising agent in the solution. This rise of potential (towards oxidising values) is not to be confused with the slight shift of potential of the peroxide itself, due to a slight decrease of P_H following upon hydrolysis of the resulting ferric salt (the potential of hydrogen peroxide being very sensitive to change of P_H in the region of neutrality). The rise of potential falls off rapidly with time in a manner nearly exponential for the first few minutes, after which a fairly steady decrease of oxidising potential persists, possibly due to decomposition of hydrogen peroxide by the ferric salt (7) or to diffusion of the junction liquid—(in these experiments saturated potassium sulphate solution). These facts will be clear from the following results.

A.—A solution of pure recrystallised ferrous ammonium sulphate was made up with freshly distilled water, containing 6·52 grm. ferrous ammonium sulphate (0·0166 mols.) per litre. This solution was freshly made up before each experiment.

A solution of hydrogen peroxide was made up from pure anhydrous hydrogen peroxide and distilled water, and adjusted so that 10 c.c. of this solution were equivalent to 40 c.c. of the ferrous ammonium sulphate solution.

10 c.c. of the hydrogen peroxide solution were added to 40 c.c. of neutral buffer solution, and the potential of a polished platinum foil electrode, treated in the usual way, and immersed in the vigorously stirred solution, was observed

FIG. 2.



against a saturated calomel electrode, using 3·5 N KCl and saturated K_2SO_4 as junction liquids.

4 c.c. of ferrous ammonium sulphate solution were added rapidly to this solution, and the potential measured at definite intervals of time.

Results (*see* fig. 2).—Measurements were made at room temperatures, the temperature of the solution being 17° C.

Time, minutes.	Observed Potentials. Volts.		(Calomel Electrode the negative pole.)
	Experiment I.	Experiment II.	Experiment III.
0	0·243*	0·246*	0·245*
	0·272†	0·274†	0·272†
½	0·268	0·2675	0·267
1	0·2645	0·2650	0·2645
2	0·2617	0·2622	0·2615
3	0·2598	0·2600	0·2597
5	0·2567	0·2573	0·2574
7	0·2540	0·2558	0·2555
10	0·2518	0·2535	0·2537
15	0·2495	0·2515	0·2515
20	0·2480	0·2503	0·2505
25	0·2473	0·2493	0·2498

* Before addition of ferrous sulph.
† After addition of ferrous sulph.

B.—The procedure in these experiments was similar, except that the hydrogen peroxide solution was kept at 0° C., the ferrous sulphate being also cooled to this temperature before addition.

Time, minutes.	Observed Potential. Volts.		(Calomel Electrode the negative pole.)
	Experiment I.	Experiment II.	Experiment III.
0	0·243*	0·243*	0·243*
	0·269†	0·267†	0·270†
½	0·266	0·2625	0·2658
1	0·264	0·261	0·2638
2	0·262	0·2595	0·2618
3	0·261	0·2582	0·2604
5	0·259	0·2565	0·2587
7	0·2577	0·2555	0·2575
10	0·2566	0·2543	0·2564
15	0·2555	0·2530	0·2553
20	0·2547	0·2522	—
25	0·2540	0·2515	—

* Before addition of ferrous sulph.
† After addition of ferrous sulph.

From these results it will be apparent that the fall of potential occurring after 20 minutes' interval takes place at the rate of 0·7 millivolts in 5 minutes, with the exception of Experiment A II, in which the rate of fall is 1 millivolt in 5 minutes.

If this steady drift be subtracted from the results given above, the curves obtained are exponential, being asymptotic to the corrected value of the potential observed after 20 minutes' interval. The following values of K have been calculated from the equation

$$\mathrm{K}\ (t_1 - t_2) = 2\cdot 3\ (\log_{10} \mathrm{E}t_2 - \log_{10} \mathrm{E}t_1)$$

where

$\mathrm{E}t_2$ = the potential, measured from the asymptote, at t_2 minutes.

$\mathrm{E}t_1$ = the potential, measured from the asymptote, at t_1 minutes,

for the intervals 1–2, 2–3, 3–5, 5–7, 7–10, 10–15 minutes respectively.

Experiments.

A I.	A II.	A III.	B I.	B II.	B III.	
0·207	0·239	0·285	0·317	0·232	0·297	Successive Values of K.
0·175	0·241	0·224	0·207	0·288	0·336	
0·177	0·196	0·175	0·288	0·226	0·255	
0·179	0·131	0·205	0·304	0·214	0·281	
0·185	0·214	0·191	0·293	0·254	0·292	
0·218	0·194		0·276		0·276	
0·196	0·205	0·215	0·281	0·242	0·290	Mean values of K.

Taking into consideration the small range of potential covered by the above figures—the average value of $\mathrm{E}t_2 - \mathrm{E}t_1$ being of the order of 2 millivolts in experiments A and 1 millivolt in experiments B—and the difficulty of measuring the potential with accuracy when it is changing with time, these results may be taken as establishing the exponential character of the curves within the limits of experimental error. It is doubtful whether much significance can be attached to the numerical values of K, since the separation of ferric hydroxide as a colloid introduces an unknown factor into the reaction, and probably modifies its velocity. Also, the assumption that the potential drift due to secondary reaction is constant throughout the earlier part of the process is at best an approximation.

Nevertheless, the results may be taken as proving definitely that the first action of hydrogen peroxide upon ferrous sulphate is the formation of a small quantity of an oxidising agent of high oxidising potential, which rapidly decomposes, either spontaneously or by reaction with excess of ferrous salt, its decomposition following the course of a monomolecular reaction (since for small concentrations the potential difference can be considered as proportional to the concentration of the oxidising agent formed). This oxidising agent cannot be other than a peroxide of iron ; though the above experiments do not furnish any evidence of its formula. The latter has, however, been established by the method of electrometric titration, carried out under the following conditions.

Experiment I.—Approximately $N/200$ solutions of hydrogen peroxide and ferrous ammonium sulphate were made up and standardised separately against acid permanganate, 10 c.c. of peroxide solution being thus equivalent to

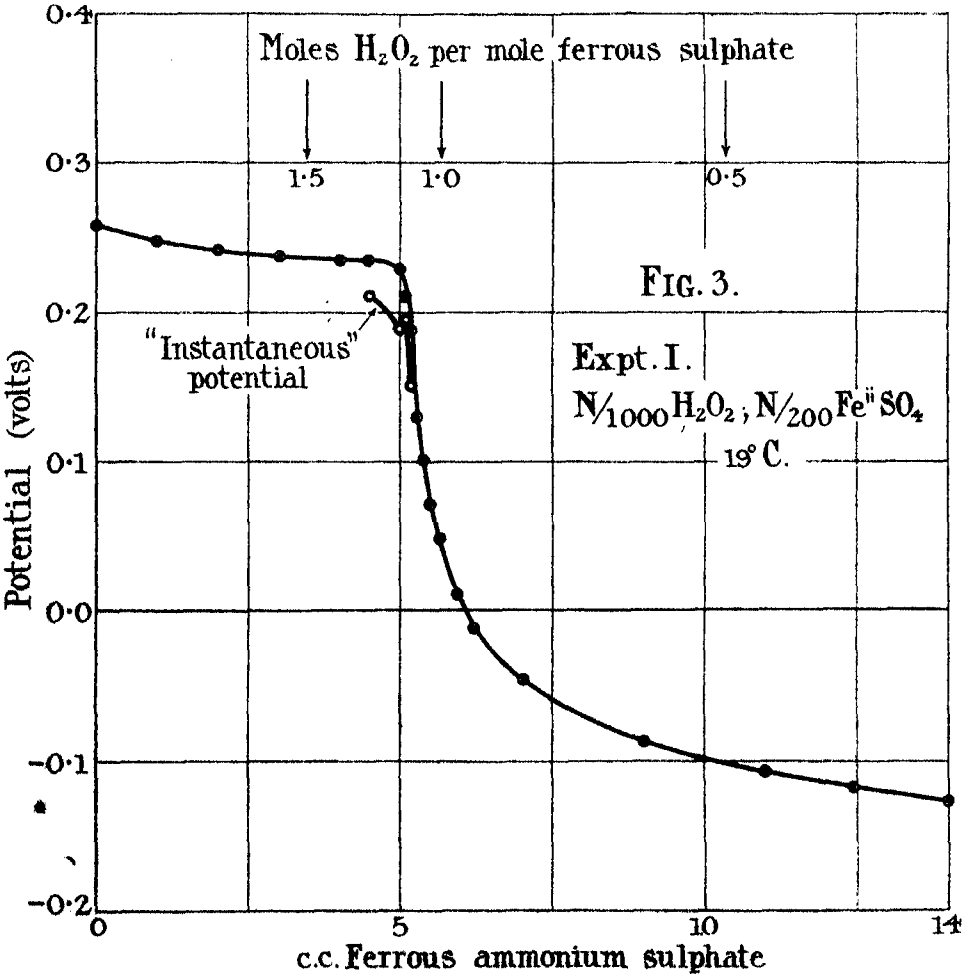


Fig. 3.

10·32 c.c. of ferrous solution. 10 c.c. of the former were then added to 40 c.c. of neutral buffer solution and titrated with the latter, the ferrous salt being run into the hydrogen peroxide slowly, while the solution was vigorously stirred. The progress of the titration was followed electrometrically, using a saturated calomel electrode, with 3·5 N KCl and saturated K_2SO_4 as junction liquids, a platinum wire electrode dipping into the solution. The temperature of the experiment was 19° C.

As a result, it was found that the end point of the titration was reached when only 5·2 c.c. of ferrous solution had been added. The approach of the end point was heralded by a sudden drop of the potential, after each addition of ferrous sulphate, followed by a recovery to nearly the initial value. This phenomenon will be further described in the sequel; it is shown graphically in fig. 3.

Experiment II.—A second experiment gave a similar result, the end point being reached at a stage corresponding approximately to the destruction of 1·0 mol. of hydrogen peroxide to 1 mol. of ferrous sulphate (instead of the proportion 0·5 : 1 necessary for conversion of ferrous iron to ferric). This relation was later found to be fortuitous, and due to the secondary reaction between iron peroxide and ferrous sulphate.

Experiments III, IV.—In these experiments approximately N/200 hydrogen peroxide and ferrous ammonium sulphate solution containing 0·00129 mol. per litre were employed. 10 c.c. of the former were placed with 40 c.c. neutral buffer solution in a small beaker surrounded by melting ice and stirred vigorously.

The ferrous solution was added slowly (about 1 drop in 5 seconds) and the potential recorded 1 minute after each addition.

In Experiment III, 10 c.c. $H_2O_2 = 37·2$ c.c. ferrous ammonium sulphate solution;

In Experiment IV, 10 c.c. $H_2O_2 = 39·12$ c.c. ferrous ammonium sulphate solution

(by separate titration with permanganate).

The result of Experiment IV is shown graphically. (That of Experiment III was identical, the end point occurring when 12·2 c.c. of ferrous solution had been added.) It will be apparent that the end point occurs at a point corresponding to the destruction of 1·5 mols. of hydrogen peroxide by 1 mol. of ferrous sulphate, and further that the end point is followed by a short approximately horizontal segment of the titration curve, which gives place to a comparatively gentle slope. This indicates beyond a doubt the presence of a very small quantity of iron peroxide in the solution undergoing titration.

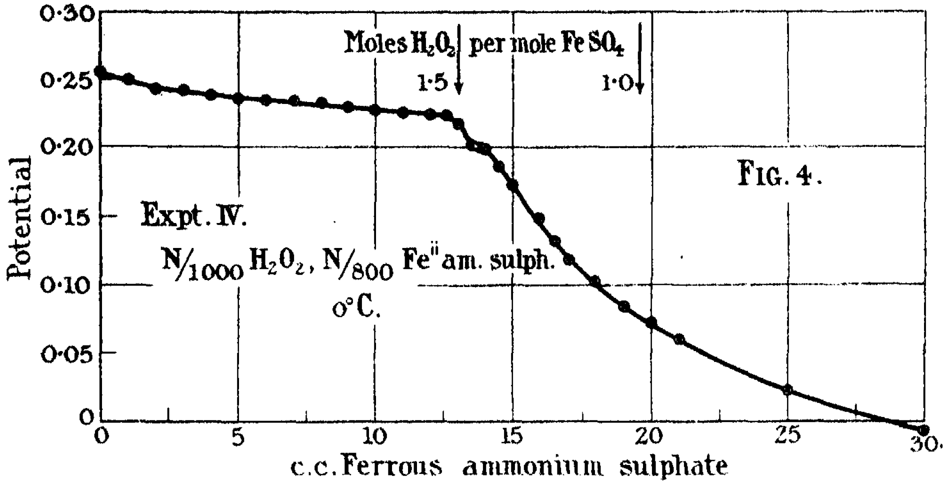


Fig. 4.

In Experiment V solutions of similar strength were employed. 10 c.c. of the H_2O_2 solution were equivalent to 37·8 c.c. of ferrous ammonium sulphate solution containing 0·00129 mol. per litre. The solution was kept at 0° C. and the potential recorded (1) as rapidly as possible, (2) 1 minute, (3) 2 minutes, (4) 3 minutes after the addition of each quantity of ferrous sulphate.

The results are expressed graphically (fig. 5).

In Experiment VI the potentials were recorded (1) 30 seconds and (2) 1 minute after each addition of ferrous sulphate. The numerical results are given here as typical of those obtained throughout.

Experiment VI.

10 c.c. H_2O_2 = 37·8 c.c. ferrous ammonium sulphate solution 0·00129 mols./litre.

10 c.c. H_2O_2, 40 c.c. neutral buffer solution. Temperature 0° C.

c.c. ferrous solution.	E obs. after		c.c. ferrous solution.	E obs.	
	(*a*) 30 secs.	(*b*) 1 min. (volts).		(*a*)	(*b*)
9·5	0·208		13·3	0·170	0·204
10·8	0·200	0·224	13·7	0·155	0·190
11·0	0·198	0·224	13·95	0·144	0·182
12·0	0·180	0·220	14·5	0·120	0·158
12·2	0·176	0·220	15·0	0·115	0·141
12·6	0·168	0·210	16·0	0·105	0·116
12·85	0·170	0·205	17·0	0·096	0·094
13·05	0·170	0·206	18·0	0·086	0·086

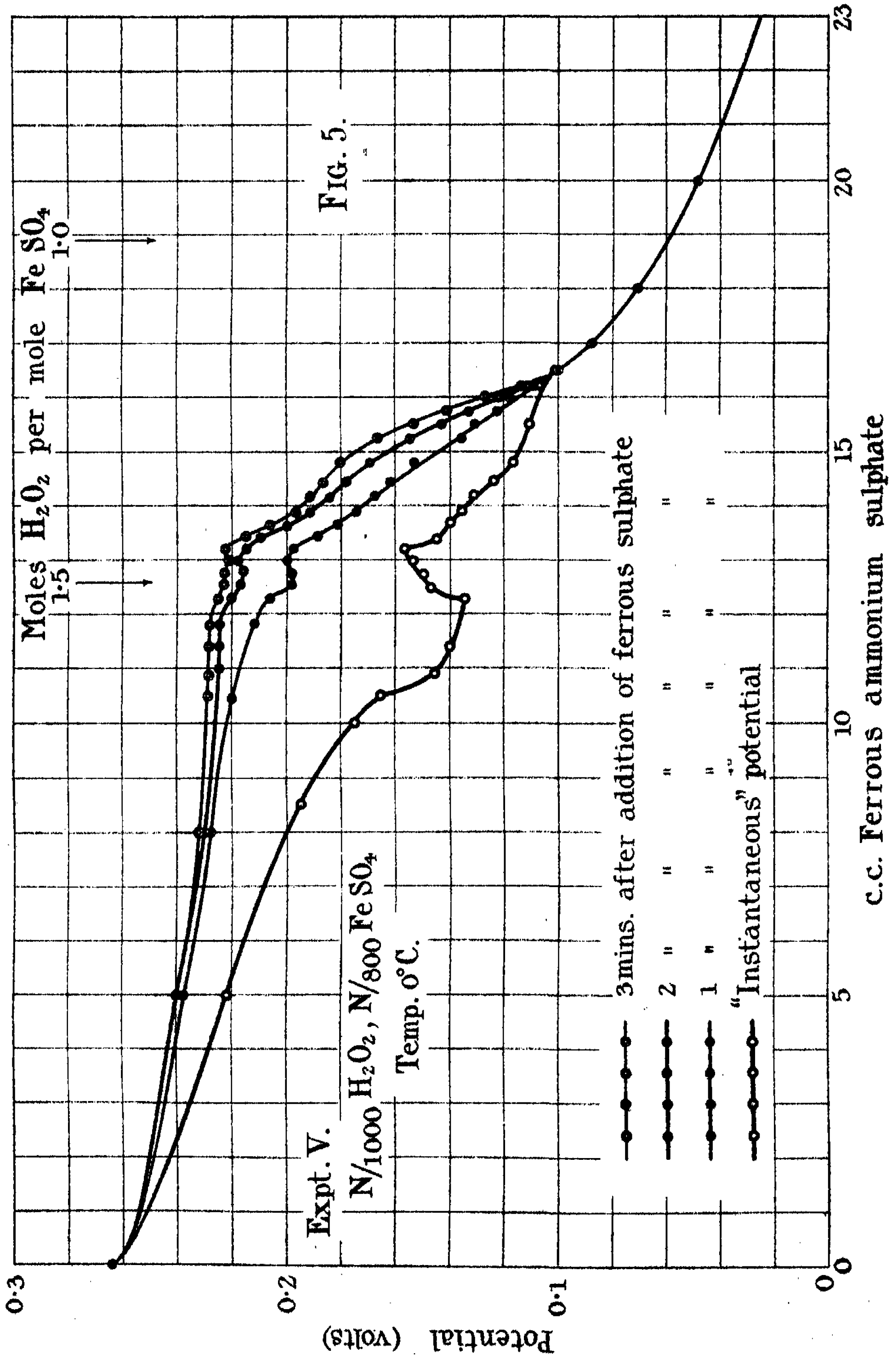


Fig. 5.

Moles H_2O_2 per mole $FeSO_4$
1·5
1·0
Expt. V.
N/1000 H_2O_2, N/800 $FeSO_4$
Temp. 0°C.
3 mins. after addition of ferrous sulphate
2 " " " " " "
1 " " " " " "
"Instantaneous" potential
c.c. Ferrous ammonium sulphate
0
5
10
15
20
23
Potential (volts)
0·3
0·2
0·1
0

About a dozen such experiments were performed and the curves obtained all exhibited similar features. They indicate beyond question that the oxidation of ferrous iron by hydrogen peroxide proceeds by the formation of an intermediate compound; since the true end point of the titration is reached at a point corresponding to the destruction of 1·5 mols. of hydrogen peroxide by 1 mol. of ferrous sulphate, this intermediate compound must therefore possess the essential formula Fe_2O_5.

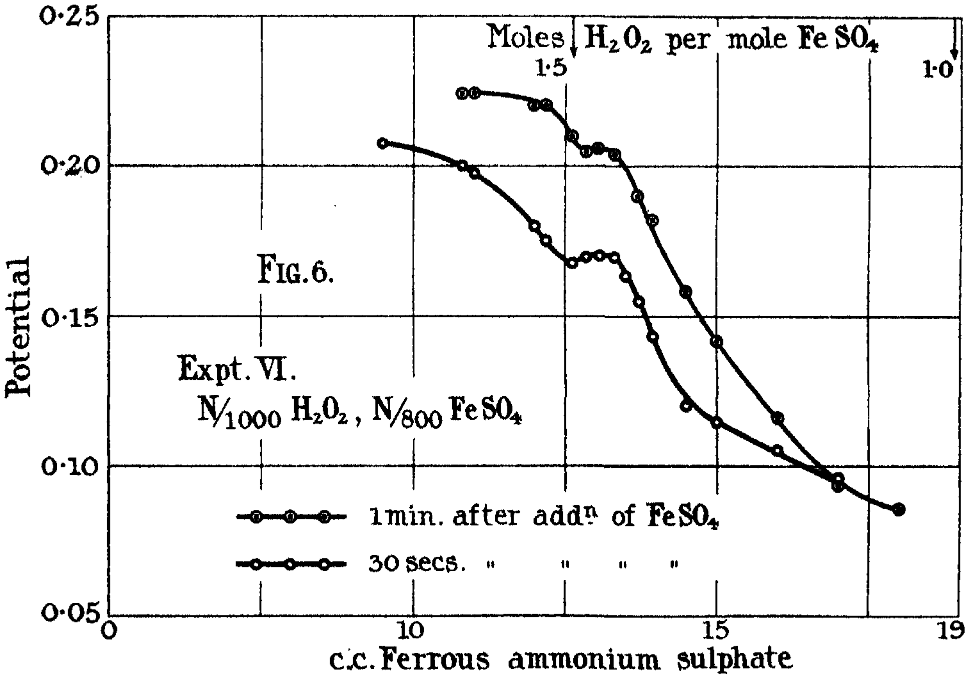


FIG. 6.

The decomposition of hydrogen peroxide, catalysed by iron salts, has been recently studied by Von Bertalan (8), Van L. Bohnson (9), and Bohnson and A. C. Robertson (10). The first-named writer found that the decomposition of hydrogen peroxide followed a monomolecular law; its velocity was proportional to the peroxide concentration and to that of the ferrous or ferric ion, inversely proportional to the hydrogen ion concentration and independent of the initial state of oxidation of the iron. This last point was confirmed by the other investigators above mentioned, who accounted for the phenomenon of decomposition by supposing the formation of ferric acid, H_2FeO_4, by the action of H_2O_2 upon ferric salt, confirming this by spectroscopic evidence.

Since the statement that the decomposition of hydrogen peroxide proceeds independently of the initial state of oxidation of the iron is contrary to the results of Manchot and Fenton, quoted in the earlier section of this paper, which have been confirmed by the potential measurements described, with the conclusion that the first action of hydrogen peroxide upon ferrous iron is the direct formation of Fe_2O_5, the point has been further investigated.

In acid solution, Manchot found that the iodine separation in Schönbein's reaction was retarded; ferrous salts nevertheless possessed a greater efficiency in this respect than ferric salts, when added under the special conditions of his experiments. This retardation of the iodine separation may be accounted for by supposing the initial formation of Fe_2O_5 to be retarded by the presence of hydrogen ions, since the ferrous ion is well known to be stabilised by acid.

Decomposition of Hydrogen Peroxide in Acid Solution.

(*a*) *By Ferrous Salts.*—The action of ferrous sulphate solution upon excess of hydrogen peroxide, working with decinormal sulphuric acid solutions, has been studied under conditions similar to those obtaining in the experiments with neutral solutions described in the previous section of this paper. The oxidation potential under these circumstances follows an entirely different course. Immediately after the addition of the ferrous sulphate, it falls, owing to the presence of ferrous iron, rising very rapidly until at the end of about one minute a slow and constant drift of potential towards more oxidising values sets in.

In acid solution there is thus no apparent evidence of the formation of an intermediate compound of high oxidation potential, as in the case of neutral solutions.

(*b*) *Decomposition by Ferric Salts.*—Similar experiments have been performed again using decinormal acid solutions, to ascertain the effect upon the oxidation potential of the addition of ferric iron, the solution employed being of pure recrystallised ferric ammonium alum. In this case the potential at once established a slow drift similar to that perceived at the end of the preceding experiments.

There was no indication of a momentary rise of oxidation potential such as would accompany the formation of an appreciable quantity of an intermediate oxide.

From these experiments it seems most probable that the decomposition of hydrogen peroxide by ferric salts is a reaction different from, and independent of, the Fe_2O_5 formation, which is the first action of hydrogen peroxide upon ferrous salts; the former may indeed quite likely be due to the formation of a very small amount of ferric acid. Further, in acid solution, in the absence of an acceptor such as potassium iodide, the Fe_2O_5 formed when ferrous sulphate is acted upon by hydrogen peroxide is reduced at once by remaining ferrous salts, giving ferric salt; while in neutral solution the Fe_2O_5 is formed sufficiently rapidly to influence a platinum electrode in contact with the solution and in sufficient quantity to cause it subsequently to decompose spontaneously. This may be confirmed by the simple experiment of adding a little dilute neutral ferrous sulphate solution to neutral hydrogen peroxide solution; after a couple of seconds a small but definite evolution of oxygen will be observed, which rapidly slackens and ceases. This phenomenon, which is due to the decomposition of Fe_2O_5, will not be observed if the same experiment be performed in acid solution.

That the decomposition of hydrogen peroxide by ferrous and ferric salts respectively takes place by essentially independent processes was further supported by a repetition of the experiments in the presence of copper sulphate. Bohnson and Robertson (*loc. cit.*) found that copper salts acted as efficient promoters of the decomposition. It was found that the copper sulphate had no effect, either upon the formation of Fe_2O_5 from ferrous sulphate in neutral solution or upon the rate of oxidation of the ferrous sulphate in acid solution. Consequently, the influence of the copper salt must be exerted upon the second reaction, that of the decomposition of hydrogen peroxide by ferric salt.

Finally, a word may be said in explanation of Bohnson and Robertson's conclusion, that the initial stage of oxidation of the iron is a matter of indifference. This conclusion may readily be seen to follow from the order of their experiments, which consisted in adding hydrogen peroxide to an acid solution of ferrous or ferric salt, shaking and observing the oxygen evolution. Under these conditions, as the writers themselves observe, the ferrous salt is instantly oxidised to the ferric state, and the latter salt alone determines the subsequent course of reaction.

SUMMARY.

1. Schönbein's reaction (the separation of iodine from potassium iodide solution in the presence of hydrogen peroxide and ferrous salts) has been investigated from the standpoint of oxidation potential and has been shown to conform to the schemes for coupled and catalytic reactions described in Part I of this paper.

2. Direct evidence has for the first time been obtained of the formation of a peroxide of iron by the action of hydrogen peroxide upon ferrous sulphate in neutral solution, and its decomposition according to a monomolecular law has been followed by means of potential measurements.

3. This peroxide has been shown, by the method of electrometric titration under special conditions, to possess the essential formula Fe_2O_5.

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(1) Manchot, 'Zeit. Anorg. Chem.,' vol. 27, pp. 397, 420 (1901); 'Ber.,' vol. 34, p. 2479 (1901); 'Liebig, Ann.,' vol. 325, pp. 93, 105 (1903).

(2) Fenton, 'Journ. Chem. Soc.' (Trans.), vol. 65, p. 899 (1894); vol. 75, p. 1 (1899); *ibid.* (Proc.), p. 119 (May, 1898). Cross, Bevan and Claude-Smith, *ibid.* (Proc.), p. 115 (May, 1898); Ruff, 'Ber.,' vol. 32, p. 550 (1899).

(3) Skrabal, 'Zeit. Anal. Chem.,' vol. 42, p. 359 (1903); 'Zeit. Anorg. Chem.,' vol. 42, pp. 48, 76 (1904).

(4) Skrabal, *loc. cit.*

(5) Mummery, 'Journ. Soc. Chem. Ind.,' vol. 32, p. 889 (1913).

(6) Peters, 'Zeit. Phys. Chem.,' vol. 26, p. 193 (1895).

(7) *Cf.* Duclaux, 'Bull. Soc. Chim. de France' [iv.], vol. 31, p. 961 (1922).

(8) Von Bertalan, 'Zeit. Phys. Chem.,' vol. 95, p. 328 (1920).

(9) Van L. Bohnson, 'Jour. Phys. Chem.,' vol. 25, p. 19 (1921).

(10) Van L. Bohnson and A. C. Robertson, 'Journ. Amer. Chem. Soc.,' vol. 45, p. 2493 (1923).

A Re-investigation of the β-Ray Spectrum of Radium B and Radium C.

By C. D. Ellis, Ph.D., Fellow of Trinity College, Cambridge, and H. W. B. Skinner, B.A., Coutts Trotter Student of Trinity College, Cambridge.

(Communicated by Prof. Sir Ernest Rutherford, F.R.S. Received 12th December, 1923.)

[Plate 1.]

An interpretation of the β-ray spectrum of radium B has already been given by one of us.* It was shown that there is strong evidence for supposing that many of the β-ray groups are due to the ejection of electrons from the K, L.... levels of the radium B atom by the action of the various homogeneous γ-rays emitted by the disintegrating atoms, the energy of the ejected electron being given by the quantum equation

$$E = h\nu - w_0,$$

where ν is the frequency of the γ-ray and w_0 the absorption energy of the level.

L. Meitner† has arrived at similar results from a study of the thorium bodies, and the general point of view would appear to be therefore correct. All the work on the radium B spectrum was based on the original measurements of Rutherford and Robinson carried out nine years ago, and it was to be anticipated that a more detailed examination with the improved technique would bring out many new points.

In a recently published paper‡ we have given an account of a determination of the absolute values of the energies of certain strong lines of the β-ray spectrum of radium B. In the present paper we describe the results of a complete re-investigation of the whole β-ray spectrum of radium B, and part of that of radium C, and we shall attempt to interpret these spectra in the light of the newer experimental material.

It is satisfactory to find that though the energy scale has been changed slightly, and many new β-ray lines have been added, all the fundamenta points in the previous investigations have been strengthened.

We shall be able to show definitely that many of the β-ray groups have energies corresponding to the ejection of electrons from the atomic levels by

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* Ellis, 'Roy. Soc. Proc.,' A, vol. 99, p. 261 (1921), and vol. 101, p. 1 (1922).

† Meitner, 'Zeit. f. Physik,' vol. 9, p. 131 (1922), and vol. 11, p. 35 (1922).

‡ Ellis and Skinner, 'Roy. Soc. Proc.,' A, vol. 105, p. 60 (1924).

γ-rays which originate in the nucleus, and that it is probable that if we add the K X-rays of the element concerned to these γ-rays, all the groups could be accounted for as being due to a similar cause. As has been already shown, the results provide a ready method of measuring the wave-length of the homogeneous γ-ray. The modification which our experiments have introduced in the energies of the β-ray groups has naturally also modified the precise values of these wave-lengths given in previous papers. There it was shown that the energies of the γ-rays showed simple additive relations between themselves and certain γ-rays measured by Rutherford and Andrade by the crystal method; in fact, that the combination principle found in the optical and X-ray spectra may be extended to these γ-rays. This result led immediately to the postulation of a set of stationary states, transitions between which give rise to the γ-rays. The modifications introduced have changed some details of this interpretation, but, on the other hand, the general correctness of this view has been greatly strengthened. But still it appears unlikely that any definiteness in our knowledge of this level structure can be obtained by a mere search for numerical agreement, at least not until the general accuracy has been greatly increased. Evidence of a more fundamental nature will have to be found before we can settle this question of the exact level structure in the nucleus.

Previous work had shown that the relative intensities of the β-ray groups due to the conversion of γ-rays in the three L levels were in disagreement with the existing data on the absorption of X-rays in these levels, but it was pointed out that in this latter case the energy of the X-rays was only just above the characteristic energies of the levels, whereas in the γ-ray case the energy is considerably above them.

The evidence on X-ray absorption has been extended by the recent work of Robinson* to the case where the energy of the X-rays is distinctly above the energies of the levels, and the results are in complete conformity with the results above on the absorption of γ-rays. Our new work has confirmed this point, but it has also shown that the relative intensities of absorption in the three L levels is still more complicated than was thought previously. We have been able to settle definitely, owing to our more accurate data, which of the L levels is concerned in the production of β-rays by the absorption of the still harder γ-rays, and the result is that the particular L level which absorbs the γ-ray most strongly is found to depend intimately on the energy of the γ-ray. The interpretation is, however, not quite direct, since it is possible that electrons may be ejected by a direct transition not involving radiation, as has been suggested by Rosseland.

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* Robinson, 'Roy. Soc. Proc.,' A, vol. 104, p. 455 (1923).

These new results do not change the general picture of the β-ray disintegration and to some extent render more plausible some of the suggestions. Important papers by Meitner* and Rosseland† have been recently published on this subject, and while it is impossible to give any detailed theory of the disintegration it is possible to give an account of its various stages, so as to include all the facts known.

In paragraph 2 we describe the experimental methods and the experimental results of the measurements of the radium B and C β-ray spectra, and in paragraph 3 we give the direct results of the interpretation. In a succeeding paper we discuss the intensities of the groups and then proceed to the most important result of this work, the deduction of the nuclear level system which is responsible for the γ-rays.

Experimental Results.

The β-rays were analysed by separating them into a spectrum by means of a uniform magnetic field. The usual focussing method of analysis was used in which traces due to homogeneous groups are obtained on a photographic plate; the details have been given in previous papers. The measurement consists in determining the strength of the magnetic field H and the radius of curvature ρ of the circular paths of the various groups. The product Hρ then gives a measure of the momentum of the β-particle, and from this the energy is calculated by the relativity formulæ.

The quantity ρ was measured in the same way as was given in our paper on the absolute measurement. In the present experiments two electromagnets were used, in one of which the uniformity of the field allowed the use of a radius of curvature ρ of from 6 to 8 cm. This was the magnet with which the absolute determination was carried out, and its uniformity was fully tested then. The other magnet only allowed the use of a radius of curvature of from 2 to 3·5 cm. This is in certain cases an advantage on account of the larger proportion of the β-rays coming from the radioactive source which are collected on the photographic plate, although, of course, the dispersion and the accuracy of measurement are diminished by its use. We estimate that the measurement of ρ could be carried out to at least 1 part in 1,000 when the larger magnet was used, and to 1 part in 500 with the smaller one.

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* Meitner, 'Zeit. f. Physik,' vol. 17, p. 54 (1923).

† Rosseland, 'Zeit. f. Physik,' vol. 14, p. 173 (1923).

In order to determine H, all that is necessary in the case of the larger magnet, the uniformity of whose field had been thoroughly tested, is that one of the β-ray lines whose absolute Hρ had been determined should give a trace on the plate. The measurement of ρ for this line then gives H accurately for the whole plate. When the smaller magnet, whose uniformity could not be so accurately tested, was used, it would not suffice to have simply one β-ray line, whose absolute Hρ was known, on the plate; but if there are two of these lines the effective H for any other line can be accurately determined by interpolation, since any lack of uniformity will be of a regular type, namely, a falling-off of the field as the edges of the pole pieces are approached. Often two such lines were not available, but in this case one of the other lines whose Hρ had been determined with the larger apparatus served as substitute. In any case, the corrections for the smaller magnet were small, and we always found that the measurements made with both magnets agreed.

Since the absolute Hρ's of the prominent lines are known to at least 1 part in 500, and the relative ρ's of the lines measured with the larger apparatus to at least 1 part in 1,000, it follows that the Hρ's of the radium B lines should be accurate to about 1 in 500. With lines measured by the smaller apparatus the accuracy is somewhat less. The energies expressed in equivalent volts have been calculated from the relativity formulæ, using $1 \cdot 769 \times 10^7$* for e/m. As a result of the peculiarities of this formula, the error in the energy is less than twice that of the error in Hρ, and becomes more nearly equal to this latter error for greater energies.

The sources used were platinum wires 0·25 mm. diameter, made active by exposure to radium emanation, and consisted, therefore, of radium B + C. In some cases a small brass plate was used instead of a wire, chiefly on account of the greater ease of preparation. The method of tipping the plate in order to obtain good focussing has already been described.

In order to know which of the β-ray lines are due to radium B and which to radium C, it is necessary to investigate the β-rays from sources of pure radium C. Such sources were obtained in the usuel way by deposition on nickel plate from a solution of the active deposit of radium in hot dilute hydrochloric acid. The use of a nickel plate is objectionable, as it is quite appreciably magnetic. The fact that the field is disturbed is shown by the fact that the β-ray lines obtained with it are slightly, but noticeably, less sharp than when a brass plate is used. However, it does not seem that this need diminish

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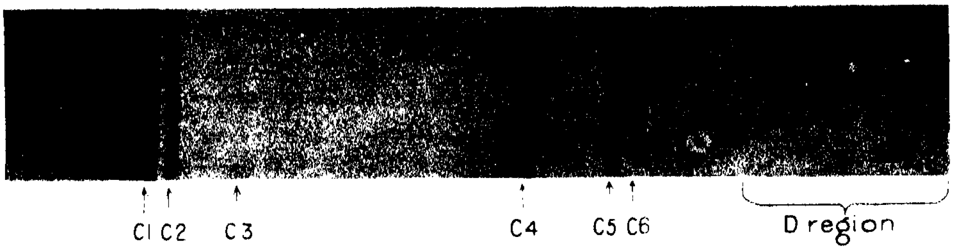
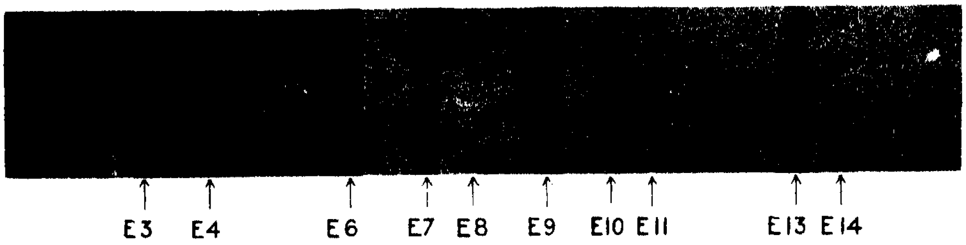
* A 1 per cent. change in the value of e/m would change the energies by $\sqrt{1-\beta^2}$ per cent., when β is the velocity of the electron.



Radium B C-Group



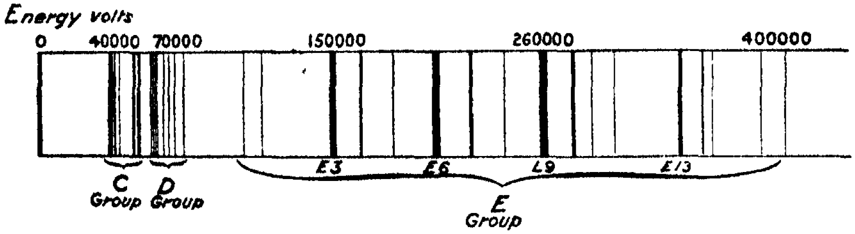
Radium B E-Group

the accuracy of the determination of the Hρ apart from the fact that owing to the less sharp character of the lines the ρ's are not quite so accurately measurable. There was always enough radium B on these sources to allow the strong radium B lines faintly to appear on the plate, and these served as calibration lines for determining H, and eliminated the disturbing effect of the nickel plate.

When the radium C lines are known the radium B lines are found by separating the radium C lines from those which have been obtained from sources of radium B + C. This part of the work was not easy, and some faint radium C lines may have been missed, and there are some faint lines whose allocation to radium B or C is rather doubtful. These doubtful lines are specially indicated in the table which follows.

Plate 1 shows reproductions of two of the plates; the details are referred to later. A diagram is also given of the entire spectrum. It can be seen that the β-ray spectrum of radium B falls naturally into three groups of lines. This separation rests entirely on an experimental basis, but we shall see that it is not without theoretical significance. In any case it suggests a natural

Diagram of Natural RaB Spectrum.



nomenclature, and we call the three groups the C, D and E groups, the C group being of lowest velocity. Then in each group we number the lines 1, 2, 3...., starting with the lowest velocity line in the group. For the radium C lines we adopt a similar nomenclature. The groups in this case are less distinctly marked off, but we take for the C, D and E groups those lines of radium C which roughly fall in the corresponding region of the radium B spectrum.

The whole of the radium C spectrum has not been reinvestigated, but only those groups of β-rays which lie within the limits of the radium B spectrum. There are many lines of greater energy than the E group lines, about which we have no new experimental data.

We have no accurate measurements of the relative intensities of the lines, but the photographic impression gives one a rough idea, and a scale is added to the lines. This does not purport to give the ratio of the lines to anything but the roughest approximation, but is convenient in showing at a glance that one line in a division is stronger than another. The estimated intensities in the C and D regions are based on direct comparison, as all these lines have been obtained on a single plate, but the relation of intensity between these regions and the E region and also between the radium B and radium C spectra is extremely vague.

A full list of the lines is given in the next table.

Table I.—β-*ray Groups of Radium B.*

Name.	Intens.	Previously accepted Hρ.	Hρ measured.	Energy volts.
C 1	8	663	660·9	$0\cdot3725 \times 10^6$
C 2	3	—	667·0	0·3792
C 3	1	—	687·0	0·4016
C 4	6	770	768·8	0·4983
C 5	4	798	793·1	0·5288
C 6	2	—	799·1	0·5365
D 1	1	836	833·0	0·5806
D 2	3	—	838·0	0·5872
D 3	1	—	855·4	0·6106
D 4	3	861	860·9	0·6172
D 5	1	—	877·8	0·6412
D 6	1	—	*896·0	0·6667
D 7	2	914	926·2	0·7094
D 8	2	950	949·2	0·7426
E 1	2	—	1155	1·068
E 2	1	—	1209	1·160
E 3	25	1392	1410	1·529
E 4	6	1470	1496	1·697
E 5	3	—	1576	1·860
E 6	30	1660	1677	2·067
E 7	8	1752	1774	2·275
E 8	3	1815	*1850	2·442
E 9	40	1925	1938	2·638
E 10	9	1990	2015	2·824
E 11	3	—	†2064	2·926
E 12	1	2140	†2110	3·033
E 13	10	2235	2256	3·379
E 14	5	2295	2307	3·502
E 15	1	—	2321	3·536
E 16	1	2450	2433	3·809
E 17	1	—	2480	3·925

* The values for these lines are less accurate.

† Possibly radium C lines.

β-ray Groups of Radium C.

Name.	Intens.	Previously accepted $H\rho$.	$H\rho$ measured.	Energy volts.
C 1	1	—	*703	$0 \cdot 420 \times 10^6$
D 1	2	—	*848	0·601
D 2	2	—	*871	0·632
D 3	1	—	*896	0·667
D 4	3	—	*944	0·725
D 5	1	—	*964	0·764
E 1	1	1380	*1379	1·470
E 2	1	1440	1438	1·582
E 3	4	1550	1557	1·819
E 4	2	—	1586	1·882
E 5	2	—	*1834	2·406
E 6	2	1918	*1912	2·580
E 7	6	2080	2085	2·975
E 8	1	—	*2156	3·142
E 9	3	2235	*2256	3·379
E 10	1	—	*2390	3·704

* The values for these lines are less accurate.

It will be seen that we have measured many new lines. In the C region we add three, one of these had already been given by Dansyz,* and again by one of us,† but its existence was not really certain. This line is marked C 2 in Plate 1 and can be seen very clearly. The value found on the old standard was Hρ 668.

The diffuse groups previously recognised to exist in the D region have proved on finer analysis to consist of a series of sharp lines comparable in every respect with the other lines; we also give two new faint ones. The C and D region of radium C is quite new. We have not found any new features in the strong lines of the E region, but besides certain new faint lines we have split up some of the previously accepted faint lines into doublets and triplets. For instance, the old radium C line Hρ 1550 has proved, on the new energy scale, to be one radium B line (RaB . E5 ... Hρ 1576) and two radium C lines (RaC . E3 and RaC . E4. . . . Hρ's 1557 and 1586). There are other examples in the tables similar to this.

The Interpretation of the Spectra.

We consider first the E region of radium B and attempt to explain it in terms of the hypothesis that the groups are due to conversion of γ-rays in the same atom that emits them.

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* Dansyz, 'Le Radium,' Jan., 1913, p. 1.

† Ellis, 'Proc. Camb. Phil. Soc.,' vol. 21, Pt. 2, p. 121 (1922).

The proof that the three strong lines E3, E6 and E9 have energies corresponding to the conversion of γ-rays in the K level of the same atom that emits them has been given in a former paper by measurements of excited spectra. We now proceed to analyse our new values as formerly from this basis, and try to account for as many lines as possible by conversion of γ-rays in the various electronic levels.

It is easy to see at once that the only lines which can be due to the conversion in the L level of those γ-rays giving E3, E6 and E9 are E7, E10 and E13. If we form the energy difference of corresponding pairs we obtain the following results :—

K — L Differences in RaB E Group.

E7 —E3	$0{\cdot}746 \times 10^5$ volts.
E10—E6	$0{\cdot}746$
E13—E9	$0{\cdot}741$

The excellent agreement of these values shows that the same L level is concerned in each case, and we may hope to find which L level by comparison with the X-ray data. Here we meet with some uncertainties. It has not been proved that the K levels of the radioactive elements are exactly identical with those of their isotopes,* but it seems reasonable that they should be, and in any case it is the only assumption which allows further calculation. Even so, the values for the K absorption energies of the heavy elements are themselves somewhat uncertain, but we take the values given recently in a paper by Bohr and Coster† with the reservation that if anything they may be too small.

Since it is possible that the γ-rays might be emitted after the disintegration when the radium B groups would really come from the radium C electronic system (atomic number 83), we give in the next table the energies of the levels for both atomic numbers 82 and 83. We also give the energies of other levels since we use them subsequently. The values taken are those given by Bohr and Coster (*loc. cit.*).

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* Rutherford and Andrade's work [Phil. Mag. (2) p. 263 (1914)] on the K spectrum of radium B shows that the K level is at least within 1 per cent. of that of lead.

† Bohr and Coster, 'Zeit. f. Physik,' vol. 12, p. 350 (1923).

*Absorption Energies.**

Atomic Number 82 (RaB).		Atomic Number 83 (RaC).
0·8752 × 10^5 volts	K	0·9000 × 10^5 volts.
0·1581	L_{I}	0·1636
0·1519	L_{II}	0·1570
0·1301	L_{III}	0·1341
0·0384 to	M_{I}	0·0401 to
0·0248	M_{V}	0·0259
0·0089 to	N_{I}	0·0096 to
0·0014	N_{VII}	0·0018
0·0014 to	O_{I}	0·0016
—	O_{V}	0·0003
0·717	$K-L_{I}$	0·736
0·723	$K-L_{II}$	0·743
0·745	$K-L_{III}$	0·766

It can be seen that our value for the separation of the K and L β-ray groups agrees with either the $K-L_{III}$ of atomic number 82 (radium B) or the $K-L_{II}$ of atomic number 83 (radium C), so that a decision on purely numerical grounds is not possible. We consider, however, that the argument advanced in a former paper to show that these lines really come from radium B electronic system is probably valid, and forms the best basis for interpretation. This argument depended on the fact that Rutherford and Andrade showed that radium B emitted an L spectrum corresponding to atomic number 82, and therefore electrons must be ejected from the L ring while the atomic number is still 82. We conclude, therefore, that in this region the prominent lines from the L level originate in the L_{III} sub-group. This is different to the conclusion reached before, where the L_{I} level was thought to be most important, but the decision depends on numerical agreement, and with the change in our energy scale the results given here seem conclusive. This brings us now as regards the E region in agreement with Meitner, who has usually used the L_{III} level in interpretation of spectra. The whole problem is complicated and is considered in more detail in the second paper.

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* The sub-groups are shown by the symbols used by Bohr and Coster, *e.g.*, L_{I}, formerly called L_3, has the greatest absorption energy, and the others are in decreasing order.

From this point the interpretation is direct and is given in the next table. The γ-ray is named by the K line it gives.

Table II.—*Interpretation of the E Group of the Radium B β-ray Spectrum.*

Name.	Intens.	Energy abs. (volts).	Energy calc. (volts).	Origin.	γ-ray.
E 1	2	$1 \cdot 068 \times 10^5$	—	K (?)	E 1
E 2	1	1·160	—	K (?)	E 2
E 3	25	1·529	1·520	K	E 3
E 4	6	1·697	1·697	K	E 4
E 5	3	1·858	—	K (?)	E 5
E 6	30	2·067	2·067	K	E 6
E 7	8	2·275	2·274	L_{III}	E 3
E 8	3	2·442	2·442	L_{III}	E 4
E 9	40	2·638	2·636	K	E 9
E 10	9	2·813	2·813	L_{III}	E 6
E 11	3	2·926	2·917	M*	E 6
E 12	1	3·033	—	L_{III}	E 12
E 13	10	3·379	3·381	L_{III}	E 9
E 14	5	3·502	3·486	M*	E 9
E 15	1	3·536	3·51 ?	N*	E 9
E 16	1	3·809	—	K	E 16
E 17	1	3·925	—	K	E 17

* It is impossible to decide which L or M level is involved.

γ-Rays of Radium B.

Name.	Energy volts.	Intens.	λ in XU.
γ E 3	$2 \cdot 404 \times 10^5$	25	51·3
γ E 4	2·572	6	48·0
γ E 6	2·942	30	42·0
γ E 9	3·511	40	35·2

Doubtful γ-rays deduced from 1 β-ray Line.

Name.	Energy.	Intens.	Name.	Energy.	Intens.
E 1	$1 \cdot 943 \times 10^5$	2	E 12	$3 \cdot 163 \times 10^5$	1
E 2	2·035	1	E 16	4·684	1
E 5	2·733	3	E 17	4·800	1

It can be seen that the main emission is due to four γ-rays, three strong and one weaker. In two cases the M lines are found in good agreement, and with the strongest γ-ray, γE9, there is evidence that a line from the N ring is present. We would scarcely expect to find an M line from the weaker γ-ray, γE4, but might reasonably have expected one from γE3. We did not find one, but it would be difficult to see, since it would lie close behind line E8 and would confound with the radium C line E5. The interpretation, as a whole, both as regards numerical agreement and relative intensity, is very satisfactory, and supports strongly the general view of the origin of the β-ray lines. Our new measurements have led both to better agreement and to a more plausible assignment of the lines, the important difference being that we now find lines from the exterior levels.

It is worth noting that with the large apparatus we could have separated groups from the L_{III} level from those from the L_I, but we found no trace of the latter lines ; they are certainly, if present at all, very much weaker than those from L_{III}.

There are six lines not accounted for, and while for one, E 12, evidence given later suggests that it may come from the L_{III} level, it is simplest to assume for the others that they are faint K lines. For the intensity of the K and L lines are always in the same sequence, the K being considerably the stronger, and if these lines had any other atomic origin one would expect to find a stronger K line somewhere on the lower energy side of it. Such lines are definitely not there in the required intensity. Thus provisionally we shall assume these lines to be K lines, and the γ-rays corresponding to them are shown in the last table. It will appear subsequently that there is a certain amount of indirect evidence for this hypothesis.

We have taken some photographs of the β-rays ejected from lead and platinum by the γ-rays of radium B, so-called lead- or platinum-excited photographs. In these experiments the source used was a fine glass tube filled with radium emanation and covered with a sheath of lead or platinum. These experiments by no means covered the complete E region, but were carried out as a general confirmation. We only took a few isolated plates with lead and no significance can be attached to our not finding certain lines.

The importance of these experiments is, firstly, that they prove that the radioactive atoms actually emit the γ-rays attributed to them. Secondly, by observing the change in energy between the natural and platinum lines the origin of the line can be found at once ; for instance, a K line from platinum should have $0 \cdot 095 \times 10^5$ volts greater energy than a K line from radium B (difference between the K absorption energies). The excited lead lines, on the other hand, should be identical with the natural lines.

These excited lines are very much more difficult to measure, because not only are they less sharp, owing to the larger source which one is forced to use, but also since it is uncertain to what portion of the source measurements should be taken, and hence there is a distinct probability of systematic error. Again the magnetic field had to be calculated from the current in the field coils, based on calibration by natural photographs. For these reasons the error in the energies may be between one-half and one per cent. While it should be possible to distinguish for radium B and platinum a K shift ($0 \cdot 095 \times 10^5$ volts) from an L shift ($0 \cdot 020 \times 10^5$ volts), no decision is possible between an L shift and an M shift ($0 \cdot 006 \times 10^5$).

Table III.—*The Energies of Corresponding Lines excited in Lead and Platinum compared with those of the Natural Radium B lines.*

Name of RaB line.	Intens.	Energy. (volts.)	Energy of Pb excited line.	Energy of Pt excited line.	Pt–RaB.	Origin of RaB line.
E 3 ………………	25	$1 \cdot 529 \times 10^5$	—	$1 \cdot 64 \times 10^5$	$0 \cdot 11 \times 10^5$	K
E 6 ………………	30	2·067	2·08	2·18	0·11	K
E 7 ………………	8	2·275	2·27	2·28	0·00	L
E 9 ………………	40	2·638	2·65	2·75	0·11	K
E 10 ………………	9	2·814	2·80	2·85	0·035	L
E 11 ………………	3	2·926	2·93	2·92	0·00	M
E 12 ………………	1	3·033	3·00	3·05	0·02	?
E 13 ………………	10	3·379	—	3·40	0·02	L
E 14 ………………	5	3·502	—	3·52	0·02	M

$$\begin{aligned} \mathrm{K(RaB)} - \mathrm{K(Pt)} &= 0 \cdot 095 \times 10^5 \text{ volts.} \\ \mathrm{L(RaB)} - \mathrm{L(Pt)} &= 0 \cdot 020 \\ \mathrm{M(RaB)} - \mathrm{M(Pt)} &= 0 \cdot 006 \end{aligned}$$

It can be seen that these experiments lend strong support to the analysis of the E region that has been advanced. The last two columns of the table contain respectively the observed separation of the platinum and radium B lines, and the origin that is attributed to the radium B line (*see* Table II). In the case of the three K lines the observed shift is in very good agreement with that calculated from the absorption energies, equally with the L and M lines the shift is sufficiently small strongly to confirm the origin given.

These experiments suggest that the unexplained line E12 is probably an L line; the corresponding K line would be at energy $2 \cdot 287 \times 10^5$ volts and intensity about 3. We did not find this line, but it would have been very close to the stronger line E 7, and may have been missed for this reason. It must be noted that the low intensity of the natural line compared to the relatively strong intensity of the excited lines makes this point rather unsatisfactory.

The C Region of Radium B.

Previous work* has shown that these groups are due to conversion of one γ-ray in the L, M and N levels, and with the new lines that we have now measured, C 2 and C 6, we have a set of six lines which by mere inspection suggests irresistibly the successive levels of the atom. This may be seen from the reproduction in Plate 1. We identify the lines as being due to one γ-ray acting on either the L_I, L_{II}, L_{III}, M, N or O levels, and attempt naturally to establish agreement with the levels corresponding to a body of atomic number 82. Here we meet with an unexpected difficulty, no agreement is found to be possible. We have calculated the minimum change in the absolute energies that would be necessary to give agreement, and believe it to be far greater than the possible error in the absolute determination, and our relative values are certainly not in error to this amount. The groups are too widely separated to correspond to atomic number 82, and the amount may be judged from the fact that if these groups did originate in an atom of atomic number 82 then relative to C 1 the group C 6 would have almost to occupy the present position of C 5, the magnitude of this shift may be seen from Plate 1. Under these circumstances it is natural to try the levels of atomic number 83 (radium C), and here we find good agreement: this is shown in the next table.

A slightly different method of presenting the results is employed here, in column 3 the observed energy is given, in columns 4 and 5 the name and absorption energy of the level in which the corresponding group is assumed to originate. Column 6 is the sum of columns 3 and 5 and representing the energy of the γ-ray should be constant if our assumptions are true.

Radium B C Group.

1 Name.	2 Intens.	3 Energy obs., volts.	4 Level.	5 Absorption energy.	6 γ-ray energy.
C 1	8	$0 \cdot 3725 \times 10^6$	L_I	$0 \cdot 1636 \times 10^6$	$0 \cdot 536 \times 10^6$
C 2	3	0·3792	L_{II}	0·1570	0·536
C 3	1	0·4016	L_{III}	0·1341	0·536
C 4	6	0·4983	M_I	0·0401	0·538
C 5	4	0·5288	N_I	0·0096	0·538
C 6	2	0·5365	O	0·0016 (?)	0·538

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* Ellis, 'Proc. Camb. Phil. Soc.,' vol. 21, Pt. 2, p. 121 (1922).

The agreement can be seen to be very good, and we take $0 \cdot 536 \times 10^5$ volts as the energy of this γ-ray. The corresponding wave-length calculated by the quantum relation is 230 XU, which is in excellent accord with one measured by Rutherford and Andrade, by the crystal method, their value being 229 XU.

We are thus confronted with a very curious conclusion. The E group β-rays and the C group γ-rays are both emitted by radium B, but while the E group are due to conversion of γ-rays in the radium B atom, the C group are due to conversion of a γ-ray in levels corresponding to those of an atom of one unit greater atomic number. In both cases it is certain that the γ-rays are emitted during the disintegration of the radium B nucleus. We leave the discussion of this point to the second paper, and desire here only to establish the result.

It is to be noted that in this group we find among the L levels the L_I to give the strongest lines; that is exactly opposite to the result found for the E group. In fact, we obtain good agreement by taking the most firmly bound of the M and N levels.*

There seems little doubt that the relative intensities of the lines from the different sub-groups undergo some curious changes in the different regions of the spectrum. In the C region the L_I sub-group absorbs most strongly; in the D region, as will be seen in the next section, the L_I and L_{III} absorb about equally, whereas, finally, in the E region the L_{III} is predominant.

We hoped to obtain some information from the excited C spectrum, but we were never able to get lines in this region. This negative result has no special meaning, however, for a calculation showed that with our experimental method extremely long exposures would have been necessary. Even if the C γ-ray were equal in strength to the main E γ-rays, which it certainly is not, it would have required six times the exposure necessary to photograph the excited E lines.

The D Region of Radium B.

When we come to analyse the D region, the interpretation is much less clear. Previous work has indicated that the faint bands found by Rutherford and Robinson in this region, which we have been able to separate up into a set of sharp lines, have energies of the right order to allow the supposition that the

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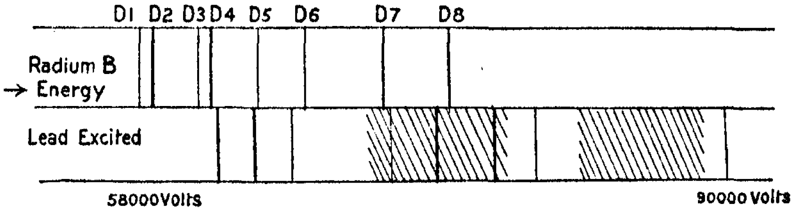
* As before, it is impossible to decide between the M_I and M_{III} levels. Had the M_{III} line been at all strong, since it would not have been separated from the M_I line, we should really have measured to it. In this case the agreement is still better. For these reasons the value of the γ-ray is taken from the first three lines.

β-rays are due to the ejection of electrons from the L levels by the K X-rays of radium B. These K X-rays are due to the ionisation of the K ring by the main γ-rays of radium B.

Our new measurements show this to be partly true, but there are lines which cannot be explained in this way. In addition, we have taken several excited photographs of lead and platinum in this region, and the results are still more difficult to interpret.

The complete evidence on the D group, with our suggested interpretation, is shown in the next table, this includes, besides the natural lines, the excited spectrum of lead. A diagram of these two spectra is also given. The diagram of the lead excited spectrum is shown with sharp lines, whereas the actual photographs show narrow bands 2 to 3 mm. wide, sharp on the high energy side and fading off on the low energy side. This is purely a result of the experimental method, the electrons ejected from the inside layers of the metal sheath being retarded in their passage out.

COMPARISON OF NATURAL AND Pb-EXCITED SPECTRA IN THE D REGION.



We consider the natural lines first.

The agreement in the table for lines D2, D4, D7 and D8 shows that these lines have energies given with good accuracy by the X-ray line $K_{\alpha 1}$, minus the absorption energies of the various levels, and since it is known that the X-ray spectrum is emitted by the disintegrating atoms it appears that at least certain fractions of these lines are due to the absorption of the K radiation in the same atom that emits it. But it is known that under normal conditions of excitation the K spectrum contains two K_{α} lines, of which the lower frequency $K_{\alpha 2}$ is at least half the intensity of $K_{\alpha 1}$, and there are also weaker β and γ lines. The weak intensity of the K_{α} group would not lead us to expect groups from the β and γ radiations, but we might reasonably expect to find the groups due to conversion of $K_{\alpha 2}$, which would be quite easily separable from the $K_{\alpha 1}$ groups. These groups are definitely not visible; we may perhaps find a reason if we consider the possibility in this particular region of radiationless transitions. That such transitions may occur in the

D Group. Radium B.

Name.	Natural lines.				Lines excited in lead.	
	Intens.	Energy obs.	Origin.	Energy calc.	Intens.	Energy obs.
D 1	1	$0 \cdot 581 \times 10^6$	$\gamma_1 - L_I$	$0 \cdot 582 \times 10^5$	—	—
D 2	3	0·587	$K_{\alpha_1} - L_I$	0·587	—	—
D 3	1	0·611	$\gamma_1 - L_{III}$	0·610	—	—
D 4	3	0·617	$K_{\alpha_1} - L_{III}$	0·615	8	$0 \cdot 629 \times 10^5$
D 5	1	0·641	$\gamma_2 - L_I$	0·640	9	0·643
D 6	1	0·667	$\gamma_2 - L_{III}$	0·668	6	0·663
D 7	2	0·709	$K_{\alpha_1} - M$	0·707 to 0·720	2	0·716 }
D 8	2	0·742	$K_{\alpha_1} - N$	0·737 to 0·744	6	0·741 } Band
	—	—	$\gamma_2 - M$	0·768	5	0·768 }
	—	—	$\gamma_2 - N$	0·793	3	0·793
	—	—	—	—	4	0·814 to 0·875 } Band
	—	—	—	—	2	0·897

$\gamma_1 = 0 \cdot 740 \times 10^5$ volts.
$\gamma_2 = 0 \cdot 798 \times 10^5$ volts.

electronic system has been suggested by Rosseland. An atom in an excited state is supposed to possess a certain probability of going to any lower quantitised state, emitting an electron with the surplus energy. Although the final energy of the electron is the same as if emission of radiation and subsequent conversion did take place, the actual details of the process are quite distinct.

Suppose, now, that at least half the electrons in these groups originate in this way, then we explain our result if transitions resulting in the ejection of an electron of energy K_{α_1}—L is far more probable than those giving electrons of energy K_{α_2}—L. Owing to our lack of knowledge of the details of this radiationless process, it cannot be said whether this is likely to be true or not, and we conclude that at present it is clearly unsafe to base any conclusions on the non-appearance of the K_{α_2} groups, and the question must be left open. Also, we can make no decision whether these lines are due to conversion or to the radiationless process.

In the last table we compared the observed energies with those calculated by subtracting from K_{α_1} the ordinary absorption energies of the L, M and N levels. To be quite accurate, we should take into account the fact that when the atom absorbs the radiation, it has one electron less than the normal number in the L_{II} sub-group. The general effect will be to make the actual absorption energies which have to be subtracted slightly greater, but the correction would appear to be less than 1 per cent. and therefore immaterial to our degree of accuracy.

We have discussed now four of the lines in the D group, and the remaining four are quite definitely not due to any K radiation acting on normal levels. They also do not appear to be due to any peculiarity of the disintegrating atom because two of them appear in the lead excited spectrum. It is clearly consistent with our general point of view to treat these lines in the same way as lines in the C or E region, that is to say, to postulate γ-rays emitted from the nucleus which by conversion in the electronic levels give these lines. It appears necessary to assume two γ-rays Dγ1 and Dγ2, which are converted in the L_I and L_{III} levels. In this region we could just separate the line from the L_{II} level, but it is so weak as to escape observation.

This might, on the whole, appear to be a satisfactory explanation of the natural D group* if it were not for the evidence afforded by the lead-excited spectrum. We should expect this last spectrum to be identical with the natural spectrum, since lead and radium B are isotopes, whereas, as the diagram shows, in fact, the dissimilarities are more marked than the similarities.

The most striking point is the occurrence of well-marked bands; these are shown in the diagram and table. Some of the lines appear to be superposed on the bands, others occur in the gaps. The excited lines themselves, although they are much broader than the natural lines, are still well defined and only about 2 mm. wide; they are quite distinct from the bands. Again, the occurrence of two separate bands decides against any explanation based on general fogging radiation. It seems necessary then to regard these bands as an actual part of the excited D spectrum. It is impossible to say whether they are real continuous bands or superposition of close lines, but in the latter case the lines cannot differ in energy by more than $0 \cdot 005 \times 10^5$ volts. We cannot offer any explanation of these bands without making very sweeping hypotheses, and will therefore consider the lines.

There are four lines which confirm strongly the existence of the γ-ray Dγ2. Groups are found due to conversion of this γ-ray in the L_I, L_{III}, M and N levels. Also in the excited platinum D spectrum we find two lines of energy, $0 \cdot 661$ and $0 \cdot 679 \times 10^5$ volts, whereas taking $0 \cdot 798 \times 10^5$ volts as the energy of the γ-ray, the calculated energies of the groups from the L_I and L_{III} levels are $0 \cdot 660$ and $0 \cdot 683 \times 10^5$ volts. From this it would appear probable that this γ-ray is emitted by the radium B nucleus, and is analogous in every respect to the other γ-rays we have found. However, we could not find any excited lines corresponding to the other γ-ray Dγ1, and, in fact, the intensity relations as a whole are unsatisfactory. After making the obvious corrections, we find that *the relative intensity of the excited Dγ2 lines to the natural lines* is too great compared to the corresponding ratio in the E region to fit in with *this explanation, unless we assume there is some special factor which makes* internal conversion of this Dγ2 γ-ray specially low.

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* The radium C D-group is not very satisfactory. We can identify two X-ray lines in excellent agreement, but the remaining three lines cannot be interpreted.

The interpretation becomes very unsatisfactory when the remaining lines are considered. We would expect to find the lines due to conversion of K_a in the L, M and N due chiefly to K and X-radiation excited in the actual lead atoms. The lead atoms are traversed by the γ-rays of radium B, which, as is shown by the existence of the E excited spectrum, eject electrons from the K rings of the lead atoms. These atoms are then capable of emitting their K spectrum, which just as in the case of the natural lines will stand a relatively large probability of being absorbed in the same atom.

If we consider the accuracy of the excited spectrum lines to be not very great, we might identify three lines as being due to K_{a1} minus L_{III}, M, and N, respectively, but it can be seen the relative intensities are not at all right, and, further, one would certainly have expected to find $K_{a1}-L_{I}$.

The explanation cannot be regarded as satisfactory, and it is also incomplete, since we are still left with the bands and the highest energy line to explain. This line appears in lead, but not in the natural spectrum, and its energy is greater than any K X-ray line. We took some photographs of the excited platinum D spectrum. It is important that we again found characteristic bands, but in different positions, and not merely shifted, as one might expect, by the L or M differences between lead and platinum. There were also indications of platinum K X-rays converted in the atom of origin. This was to be expected as in the lead case.

These excited spectra present very difficult problems, and we have not been able to give any convincing explanation on ordinary ideas. It seems almost necessary to introduce some new hypothesis, and in this case it is natural to turn to the nucleus, especially in view of the existence of lines of higher energy than any of the K X-rays of lead and the difficulty of supposing these lines to be due to mere conversion of γ-rays from radium B. It might be expected that we could obtain an explanation if we allowed ourselves hypotheses about the lead nucleus being excited by the hard γ-rays to emit radiation in the same way that its K radiation is excited. We have considered an explanation on these lines, and found it quite competent to explain all the facts, but we will not put forward the details until there is some definite evidence to justify bringing in the nucleus at all.

The E and C Regions of Radium C.

We have given new measurements of the radium C groups up to Hρ 2400. The analysis is in this case far more difficult, since probably owing to the general faintness, many fewer lines were found, and also accurate measurement was more difficult for the reasons already given.

We are guided entirely by analogy with the radium B spectrum, and suggest the γ-rays shown in the next table, which also shows the extent to which agreement is obtained with the experimental values.

The γ-rays of radium C have already been discussed by one of us. The

Interpretation of the Radium C (At. No. 83, see Table I), C and E Region.

Name.	Intens.	Energy obs., volts.	Origin.	γ-ray name.	Energy calc. volts.
C 1	1	$0 \cdot 420 \times 10^5$	L_I	C 1	—
E 1	1	1·470	K	E 1	—
E 2	1	1·582	K	E 2	—
E 3	4	1·819	K	E 3	1·82
E 4	2	1·882	K	E 4	—
E 5	2	2·406	K	E 5	2·39
E 6	2	2·580	L_{III}	E 3	2·59
E 7	6	2·975	K	E 7	2·96
E 8	1	3·142	L_{III}	E 5	3·16
E 9	3	3·379	K	E 9	—
E 10	1	3·704	L_{III}	E 7	3·73

Lower Energy γ-rays of Radium C.

Name.	Intens.	Energy, volts.	Wave-length in XU.
E 3	4	$2 \cdot 72 \times 10^5$	45·3
E 5	2	3·29	37·5
E 7	6	3·86	32·0

Doubtful γ-rays (based on one line only).

C 1	1	0·59	
E 1	1	2·37	
E 2	1	2·48	
*E 4	2	2·78	
*E 9	3	4·28	

* Calculation shows that the 2 lines of these γ-rays would have been masked by other lines, strong lines of radium B in this case, which was always present to a small extent on the radium C sources.

list given then included the first and third of these γ-rays, and also three higher energy ones (energies 4·96, 5·83, and 6·07 × 10^5 volts). The existence of the last one was made certain by excited spectrum measurements, whereas the other two were deduced from the K—L separation. We do not include these in this paper because we have not verified the energy scale in this region.

We give five γ-rays under the heading "doubtful γ-rays," which are based on one line only. We only suggest these values in view of the fact that if it is important to have some values for the γ-rays of radium C, then until more detail has been obtained all that can be done is to interpret these single lines as originating in the K ring and calculate the γ-ray accordingly. If this were true, we could scarcely have expected to find the L lines owing to their faintness. In the same way C1, the only representative of the C group would be assumed in analogy with radium B to come from the L_I level of an atom of atomic number 84, although this only involves a difference of 0·006 × 10^5 volts. We include these suggested γ-rays with the more certain ones for convenience.

On the whole, we may at least say that there is at the moment no evidence in the radium C spectrum which is incompatible with the general principles of interpretation used for the radium B spectrum.

In conclusion, we would like to express our great indebtedness to Professor Sir Ernest Rutherford for his continual help and advice, and to Mr. G. R. Crowe for the preparation of the active sources used. We also thank the Government Grant Committee of the Royal Society for a grant to one of us, which defrayed part of the cost of the apparatus used in this research.

Summary.

1. The complete β-ray spectrum of radium B has been remeasured and many new lines found.

2. The radium C β-ray spectrum has also been reinvestigated up to Hρ 2400.

3. The conclusion reached from previous work has been confirmed that these groups are due to conversion of γ-rays in the various electronic levels. This makes it possible to deduce the wave-length of the γ-rays from the β-ray measurements.

4. Whereas the majority of the β-ray lines from radium B (atomic number 82) are due to conversion in atoms of this atomic number a group of low energy radium B lines has been found to be due to conversion in atoms of atomic number 83.

5. The relative absorbing powers of the different L sub-groups changes with the frequency of the absorbed γ-ray.

The Interpretation of β-Ray Spectra.

By C. D. Ellis, Ph.D., Fellow of Trinity College, Cambridge, and H. W. B. Skinner, B.A., Coutts-Trotter Student of Trinity College, Cambridge.

(Communicated by Prof. Sir E. Rutherford, F.R.S. Received December 12, 1923.)

In the preceding paper we have described the results of a detailed re-examination of the radium B and radium C β-ray spectra, and also from these spectra we deduced the energies or wave-lengths of the γ-rays emitted by these bodies. There is, however, a great deal more information that can be obtained from these measurements. It is admittedly of a less certain character but refers to very important problems. It is the object of this paper to describe these further deductions.

In the first section we discuss some details connected with the ejection of the natural β-ray groups. In the second section we confirm the conclusion reached from previous work that there are stationary states in the nucleus, of which the energy differences can be obtained from the γ-rays measured. Here we find the new and interesting result that there seem to be striking analogies between the level systems of radium B and radium C. Finally, a short discussion is given of the bearing of our general results on the theory of the β-ray disintegration.

Mechanism of Ejection of the Natural β-ray Groups.

In the preceding paper, in discussing the β-ray groups, both natural and excited, we have always adopted the view that they were due to the conversion of γ-rays. This is certainly correct in the case of the excited spectra where the γ-ray is emitted by one type of atom, radium B, and absorbed by another, lead or platinum. Since, however, radium B emits exactly similar β-ray groups to those ejected from its isotope, lead, by the γ-rays of radium B, it is natural to assume that the radium B β-ray groups are also due to the same process. In this case, as has been often pointed out, there are so few radium B atoms present, that this conversion must occur in the same atom that emits the γ-ray.

We regard this as the best and simplest view to take of the origin of these groups. There is another view that might perhaps be held, and we think it important to point out that even if this second view were true it would not affect the general deduction of the γ-rays and the nuclear level systems. We refer to the radiationless transitions considered by Rosseland, and already mentioned in the previous paper in connection with the D group. These transitions had to be taken into account in that region since we were there concerned with only one system, the electronic system. If it were believed that there were strong coupling between the nucleus and the electronic system, then a similar type of explanation might be applied to the main β-ray groups in the E region. There is good evidence for the existence of quantum levels in the radium B nucleus, and we are led to assume that the radium B nucleus starts its existence in one of a series of higher energy states (excited states). For example, we may say that there is a particle in a higher energy nuclear level. This alternative view would now suggest that the atom as a whole (nucleus and electronic structure) may now undergo a transition, the final state being the nuclear particle in a lower energy state and one electron from the external electronic structure ejected clear of the atom. The energy of the ejected electron will clearly be the same as if a γ-ray had first been emitted by transition between the two nuclear levels, and then subsequently absorbed in the external electronic system. Hence whichever may be the correct view of the origin of the natural β-ray groups, we still, by our analysis of them, do deduce the energy differences of the stationary states in the nucleus, and that is the really important result of these measurements.

This radiationless theory of ejection may have application to X-ray phenomena, or to a process which is entirely confined to the nucleus, but we do not think it can apply to the main β-ray groups of radium B. We believe these to be due to emission of radiation from the nucleus and subsequent conversion. We feel that at the moment the general evidence indicates that the nucleus is so distinct from the electronic system that the only method of transferring energy from one to the other is by radiation.

The Intensities of the Groups.

When we discuss the general intensities of the lines the point of view becomes very important. The β-ray spectra show the intensity of the different groups relative to the number of atoms disintegrating. An atom about to disintegrate is in an excited state, and leaving aside the disintegration electron and multiplicity of γ-ray emission, emits either a γ-ray or a β-ray line electron. We find the number of β-ray line electrons to be extremely high, so that believing them to be all due to internal conversion of the γ-ray, we deduce that this internal absorption coefficient has a very high value.

The intensity measurements by the ionisation method of the natural β-ray groups of radium B show independently of any hypothesis that the total number of electrons in the three strong lines (E3, E6, E9) is at least of the order of one-tenth of the number of atoms disintegrating. This figure is obtained simply from the dimensions of the apparatus. Again, the average γ-ray energy emitted per atom disintegrating is from the measurements of Moseley and Robinson* about 1×10^5 volts. Since the average quantum of the γ-rays giving these three β-ray lines is 3×10^5 volts, it would appear that one quantum of one or other of these three γ-rays is emitted for every three atoms disintegrating. We may remark that reference to the level system of the radium B nucleus given later shows in agreement with this estimate that the total number of quanta of these γ-rays must be of the same order as the number of atoms disintegrating. Hence, out of ten atoms disintegrating, one electron is contributed to one of these three β-ray groups and in all about three quanta of radiation escape from the atom. Even allowing a factor for uncertainty in the data, we can say that at least one β-ray line electron is obtained for every ten quanta emitted.

Hence if we take the internal conversion view of the origin of these β-ray groups, then the probability of internal absorption of the γ-rays is at a moderate estimate one-tenth.

By making special assumptions about those properties of radiation on which absorption depends we can calculate the value of the probability of internal absorption from the value of the ordinary absorption coefficient, which is known for these γ-rays from direct measurements. We have tried the assumptions that the probability of absorption is proportional to either the intensity of radiation or the density of radiation at the place where the absorption occurs (the K ring), and, further, a pure light dart hypothesis in which the probability is simply equal to the chance of hitting an area round the ring where absorption takes place. All these assumptions give values far too small, the best is the light dart one and that is fifteen times too small.

There seems to be here a very definite problem to account for the observed high value of the internal absorption.

Other interesting intensity problems occur when we consider the relative strength of the groups due to conversion of the same γ-ray in different levels. The ratio of the intensities of the K lines to the L lines in the E region is about what one would expect from the ordinary λ^3 law, and in the C region the intensities of the L, M, N groups are also in general accordance. It is not until we consider the relative absorbing powers of the L level sub-groups that we meet with more complicated phenomena.

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* 'Phil. Mag.,' vol. 28, p. 327 (1914).

In the C group of radium B, where a γ-ray of energy $0 \cdot 54 \times 10^5$ volts is converted in the three L levels of energies about $0 \cdot 15 \times 10^5$ volts, we find that the intensity of the L_I group is by far the greatest and those of the L_{II} and L_{III} follow in that order on a very sharply descending scale. At first sight this result appears to conflict with the available material on X-ray absorption in which the absorption in the L_{III} always appears the heaviest. But all these absorptions really refer to absorption of radiation, whose quantum energy is only just above the characteristic energy of the level, and in the γ-ray case it is considerably above, so there is no real conflict. Also in a recent paper Robinson* has shown by analysing the electrons ejected from a target by homogeneous X-rays in a magnetic field, that as the energy of the L levels recedes below that of the radiation (kept constant) the relative importance of the three L levels in absorbing radiation suffers marked changes. When the energy of the radiation is only just above that of the level the L_{III} level is the most important, but when it is considerably above it then the L_I level becomes predominant. This is seen to be in precise conformity with our result with γ-radiation. Here we find no cause to suppose that the relative importance of the three L levels depends at all on the fact that the absorption of the radiation is internal, because in Robinson's work, of course, only external absorption was in question.

Our new measurements have enabled us to go further than this. We have mentioned that experimentally the β-ray spectrum of radium B falls into three regions which have been called the C, D and E regions. These regions have also been found to correspond to different relative probabilities of absorption in the three L levels. We have given the result in the C region. In the D region there appear to be radiations of energy of about $0 \cdot 75 \times 10^5$ volts, and these eject electrons from the L_I and L_{III} levels. The strength of the lines from the L_I and L_{III} levels are about equal, but the line due to ejection of electrons from the L_{II} level does not appear, although we should probably have found it if it had been as much as one-fourth as strong as the L_I line. Further, in the E region, where the γ-rays have energies from $2 \cdot 0$ to $3 \cdot 5 \times 10^5$ volts, we find a different order of relative absorbing powers. Although here the L_I and L_{II} lines would not be separable, they should be separable from the L_{III} line, and should be seen if they existed in any strength greater than approximately one-tenth of the strength of the L_{III}

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* Robinson, 'Roy. Soc. Proc.,' A, vol. 104, p. 455 (1923).

lines. No such lines are found, and we must conclude that this type of ejection is relatively improbable, and we revert back to the conditions holding near the absorption edge where the L_{III} level is predominant. We can sum up these results in a table, in which where a level is put in brackets, it means that the corresponding line was too faint to be seen.

Relative Absorbing Powers of the L Sub-groups for Different Radiations.

Region.	Energy of γ-ray.	Order of Intensity.
Absorption Limit	$0 \cdot 16 \times 10^5$ volts	L_{III}, L_{II}, L_I.
C	0·54	L_I, L_{II}, L_{III}.
D	0·8	L_I, L_{III} (L_{II}).
E	3·0	L_{III} (L_{II}, L_I).

Adopting the view that the natural lines are due to internal conversion of γ-rays, the agreement with Robinson's result would lead us to expect no disturbing effect from the absorption being internal, and our extended results might therefore apply to the absorption of radiation in general.

Stationary States in the Nucleus.

It was deduced from the old measurements that the emission of the γ-rays of radium B resulted from transitions between stationary states in the nucleus, and it is necessary to verify that this conclusion is still true with the new energy values.

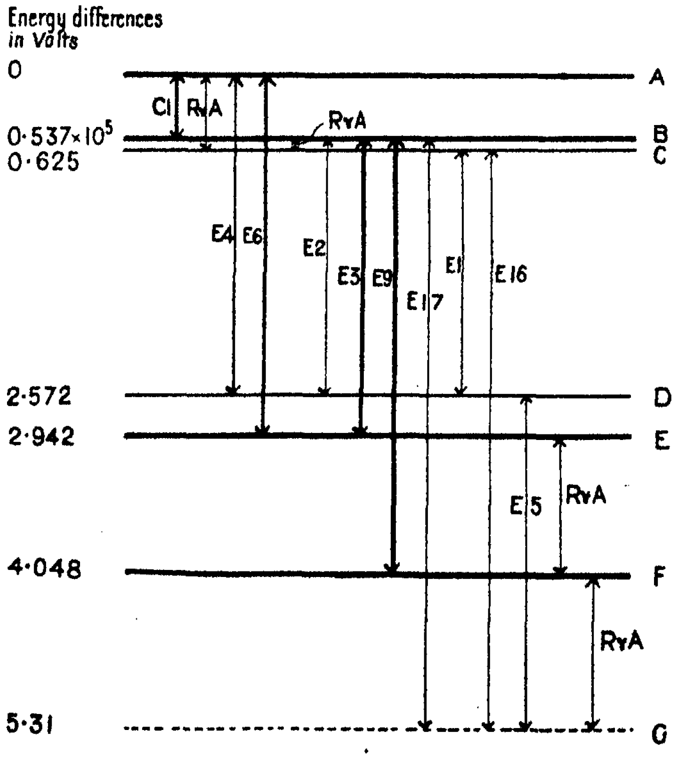
It has been shown in the preceding sections that, in addition to certain other rather doubtful γ-rays, radium B certainly emits the following γ-rays. It is not necessary to repeat the reasons for believing them to come from the nucleus.

γ-rays of Radium B.

Intensity.	Name.	Energy in volts.
8	C 1	$0 \cdot 537 \times 10^5$
25	E 3	2·404
6	E 4	2·572
30	E 6	2·942
40	E 9	3·511

It can be seen that the difference between γE6 and γE3 is $0 \cdot 538 \times 10^5$ volts, which is almost identical with the energy of γC1. Again, the difference between γE9 and γE3 is $1 \cdot 107 \times 10^5$ volts, corresponding to a wave-length of 111·5 XU, is in fair agreement with a γ-ray measured by Rutherford and Andrade* by the crystal method, their value being 115 XU. Further, we gave reasons to believe that the β-ray line E2 came from the K level, and was due to a γ-ray γE2 of energy $2 \cdot 035 \times 10^5$ volts, which again shows the difference of $0 \cdot 537 \times 10^5$ volts from γE4. The first of these three combinations is absolutely certain, and we add the other two as strong confirmatory evidence. The simplest way of explaining these combinations is to assume, what is in itself intrinsically probable, that the quantum dynamics apply to the nucleus, and that the emission of these γ-rays is due to transitions between stationary states characteristic of the radium B nucleus. The determination of the exact structure of the set of levels is not possible with any certainty because the γ-rays themselves have not been measured sufficiently accurately to distinguish between different systems. We give one possible arrangement in Diagram 1,

Diagram 1.—Energy Levels of the RaB Nucleus.



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* 'Phil. Mag.,' vol. 2, p. 263 (1914).

which is quite similar to the one given in a former paper. The four levels, B, D, E and F, take into account the combinations already described, involving eight γ-rays. If we add a close companion level C to B, we include three other γ-rays, of which one E1 is suggested by the occurrence of a single line in the β-ray spectrum, and the other two agree with crystal measurements of Rutherford and Andrade. In the same way, another level 6 may be added. The numerical agreement is shown in the next table. All the radium B γ-rays except one (E12) are given by this system.

Possible Nuclear Level System of Radium B.

Transition.	Energy calc.	Energy obs.	How measured.
A–B	0·537	0·537	β-ray spectrum, confirmed by R. and A.
A–C	0·625	0·629	Crystal, R. and A.
A–D	2·572	2·572	β-ray spectrum.
A–E	2·942	2·942	β-ray spectrum.
A–F	—	not observed	
A–G	—	not observed	
B–C	0·088	0·090	Crystal, R. and A.
B–D	2·035	2·035	β-ray spectrum (one line only).
B–E	2·405	2·404	β-ray spectrum.
B–F	3·511	3·511	β-ray spectrum.
B–G	4·773	4·800	β-ray spectrum.
C–D	1·947	1·947	β-ray spectrum (one line only).
C–E	—	not observed	
C–F	—	not observed	
C–G	4·685	4·684	β-ray spectrum.
D–E	—	not observed	
D–F	—	not observed	
D–G	2·738	2·733	β-ray spectrum.
E–F	1·106	1·073	Crystal, R. and A.
E–G	—	not observed	
F–G	1·26	1·25	Crystal, R. and A.

We consider that the evidence as a whole is strongly in favour of the fact that the quantum dynamics apply to the nucleus, and we think that the level system proposed here is sufficiently probable to form the basis of some further discussion, but we wish to again emphasise the difficulties and uncertainties in setting up a level system merely by looking for numerical coincidences.

It will have been noticed that we have included the γ-ray γC1 with those of the E group, although, as was shown in the previous paper, while the latter give β-ray groups from atoms of atomic number 82, the former is converted in atoms of atomic number 83. It has already been pointed out, however, that the β-ray groups defining all these γ-rays undoubtedly come from the disintegrating radium B1 atoms, and it is certain that the C1 γ-ray and the E group γ-rays are all emitted from the radium B nucleus during the disintegration. These facts, joined with the excellent numerical agreement shown by the combination differences, justify the step of combining them into one level system characteristic of this nucleus, and we are left with the problem of accounting for the reason why they are converted in extra-nuclear levels of different atomic number.

It is clear at once that in this problem we are concerned with the ordering of a series of events relative to the exact instant of the emission of the disintegration electron. For instance, we could express our results by saying that the E group γ-rays are emitted before the disintegration, but the C1 γ-ray after this event. This, of course, introduces new difficulties, but we instance it to show that in this problem we must take into consideration the exact sequence of events in the disintegration. This question may become very important, and we must point out that the whole argument depends on the statement that the E group γ-rays are converted in levels corresponding to atomic number 82, which in turn depends on the fact that Rutherford and Andrade observed that radium B emitted the L X-ray spectrum during its disintegration.* If any other way of explaining this fact is devised, then the considerations that follow must be revised.

There are many attitudes that could be taken towards this fact; we might, for instance, suppose that the electronic levels had the power of holding absorbed radiation for a finite time before emitting the electron, and that this time was greater the smaller the energy of the radiation. Thus all the γ-rays would be supposed to be emitted before the disintegration, but in the case of the C1 γ-ray the absorbed radiation is held until after the disintegration. It appears to us, however, that the most direct interpretation at the moment of this fact alone is to consider the disintegration electron to be in such a position in the nucleus that its removal alters the energy value of the B and A states to approximately the same extent. In this case we are free to assume that whereas the majority of the transitions occur before the emission of the disintegration, there is such a coupling that the transition B–A always occurs after this event. This involves the subsidiary hypothesis that the transitions occur in the direction G to A, and, further, that the B and A levels on which the

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* Ellis, 'Proc. Roy. Soc.,' A, vol. 101, p. 15, 1922. Evidence in support of this is furnished by the D group of RaB, when we find lines due to the conversion of the normal K X-rays of RaB in the normal L levels. This shows the 82 levels persist after the conversion of the E group γ-rays.

E γ-rays end are not exactly the same as the B and A levels involved in the emission of γ C1.

If we now consider the γ-rays of radium C we find a fact which may be significant. The radium C E group γ-rays are very similar to the radium B E γ-rays, but they are all about 0·3 to 0·4 × 10^5 volts greater energy. This can be seen from the next table.

Comparison of the RaB γ-rays with those of RaC.

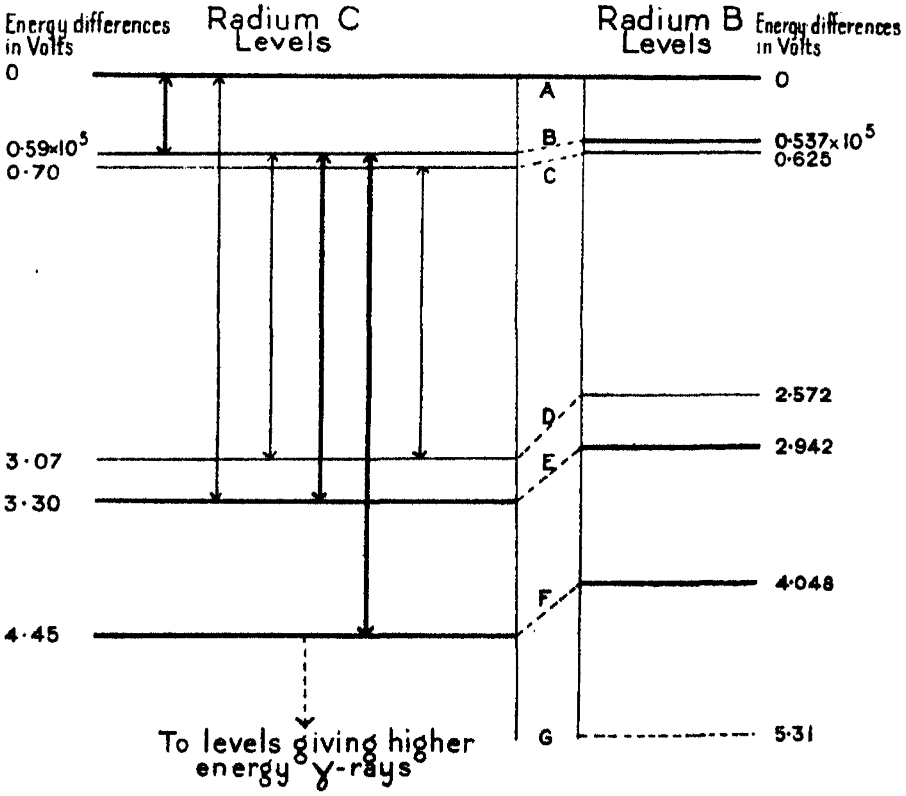
Radium B.		Radium C.		Difference.
Intens.	Energy volts.	Intens.	Energy volts.	
2	1·943 × 10^5	1	2·37 × 10^5	0·43 × 10^5
1	2·035	1	2·48	0·45
25	2·404	4	2·72	0·31
—	—	2	2·79	
4	2·572	—	—	
3	2·733	—	—	
30	2·942	2	3·29	0·35
40	3·511	6	3·86	0·35

In connection with this table, we would remark that it might be more correct to combine the fourth radium C γ-ray with the third radium B, one giving a difference of 0·39 × 10^5 volts, and, again, that a radium C γ-ray corresponding to the fifth radium B γ-ray could never be detected, even if it existed owing to the overlapping of β-ray lines. The intensities are very rough, and there is no correspondence between the radium B and radium C scales.

If we bear in mind the difference in intensity between the radium B and radium C lines, the differences are sufficiently constant to be striking, especially if we consider the correspondence of the strong lines. The lack of constancy is outside the error of measurement, but there seems to be some basis for a direct comparison. We should expect, of course, that the γ-rays of radium C are emitted by transitions between a set of stationary states, and the result we have just given suggests that this level system would show similarities with that of radium B. Something of this sort appears to occur.

We therefore try to fit the γ-rays of radium C into a level system of the same character as that of radium B, with the result shown in the next diagram. It is important that we again find the combination between the A, B and E levels; the difference between E5 (3·29 × 10^5 volts) and E3 (2·72 × 10^5 volts) does agree well with the suggested C γ-ray 0·59 × 10^5 volts. We have not included all the γ-rays, but these results do suggest now that the radium C level system has the same structure as that of radium B. This fact alone is of very great importance. It is probably independent of the actual level system used as illustration, since, finally, it depends on the similarity of the β-ray spectra. A subsidiary but very important point is that the energy differences have increased progressively. There is presumably a similar dynamical system in the radium C nucleus to that in radium B, but the field in which it moves has changed.

Diagram 2.—Energy Levels of the RaC Nucleus.



There is not sufficient evidence to justify speculation on the cause of this energy increase at the moment, but we would like to point out the following considerations. If we accept the hypothesis that the emission of the radium B disintegration electron affects the B and A levels to the same extent (and this was the most obvious assumption to account for the facts) then we have to find some cause other than the mere emission of the disintegration electron to explain the increased energy differences in the radium C level system.

This is rather a disadvantage of that particular hypothesis. Again, the radioactive disintegration is a steady progress to lower nuclear energy states, and either we must assume that all the radium B level systems do not emit γ-rays, but a few are left over in an excited state and emit in the radium C disintegration, or we must think that first one particle does the radium B transitions and then a second particle does the radium C transitions.

We have included these considerations with a view of showing that these nuclear levels may give important information, even if their energy values cannot be obtained to a high accuracy. This appears in connection with another point which we consider to be of considerable importance. In these nuclear level systems we find transitions occurring which involve very small energy differences. For instance, in the radium B levels the existence of the transition B–A of 54,000 volts (fig. 1) is made quite secure by the occurrence of the prominent γ-ray C1, and, again, there is quite good evidence for a transition C–B, involving an energy difference of only 9,000 volts. These small values taken in conjunction with the consideration that in the nucleus we expect to find intense fields giving rise to high energy γ-rays like the E group makes the occurrence of these transitions very interesting.

In the nuclear levels it is not yet possible to assign quantum numbers to the various states, but in the radium B set, for example, one would not anticipate each level to be characterised by a different total quantum number; far more, one would expect A, B and C to be sub-groups having the same total quantum number, and probably D, E and F at least to be also sub-groups with another quantum number. From this point of view, these peculiar low-energy transitions would appear to be between sub-groups having the same total quantum number.

Conclusion.

In a recent paper Meitner* describes some experiments on the β-rays of uranium X_1. She finds a well-marked group of three lines and also a band. The groups differ in energy by amounts clearly indicating conversion in the L, M and N levels, and she deduces a γ-ray which lies midway between the $K\alpha_1$ and $K\alpha_2$ X-ray lines. For this reason she concludes that uranium X_1 emits its K X-ray spectrum, and since it shows no other lines, this must be the only type of radiation emitted. The band she interprets as consisting of disintegration electrons, which owe their inhomogeneity to the varying losses of energy they suffer in exciting the K X-radiation by direct collision, as they leave the atom. But for this the electrons would come out with a definite energy, like the α-particle. The views we hold are not easily reconcilable with this type of disintegration in all its details, but leaving this question aside for the moment we would suggest that there is another way of interpreting these experimental facts.

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* Meitner, 'Zeit. f. Physik,' vol. 17, p. 154 (1923).

We cannot see that it is correct to expect the β-ray lines to correspond to the average value of $K\alpha_1$ and $K\alpha_2$, as Meitner does. Even if both these radiations were emitted, and the corresponding groups could not be separated, it follows from the experimental arrangement that the part of the photographic trace to which measurements are taken would correspond to the harder component and not to the mean of these two. She finds the β-ray line from the L level to have an energy of $0 \cdot 711 \times 10^5$ volts, and the energies of the lines that would be due to the X-ray radiations are as follows :—

$$\begin{array}{llll} K\alpha_1 - L_I = 0 \cdot 692 \times 10^5 \text{ volts.} & & K\alpha_2 - L_I = 0 \cdot 726 \times 10^5 \text{ volts.} \\ \quad\;\; - L_{II} = 0 \cdot 700 & & \quad\;\; - L_{II} = 0 \cdot 734 \\ \quad\;\; - L_{III} = 0 \cdot 734 & & \quad\;\; - L_{III} = 0 \cdot 768 \end{array}$$

$$(K\alpha_1 = 0 \cdot 8967 \times 10^5 = 0 \cdot 9306 \times 10^5 \text{ volts.})$$

Our results tend to show that conversion in the L_{II} level is relatively improbable, but we have included these lines. Her measurements were certainly not one per cent. in error, and there is no agreement at all; and in general had these groups been present one would have expected to see them as a narrow band extending down from $0 \cdot 768 \times 10^5$ volts to lower energies. We cannot see that there is any evidence at all that the X-ray spectrum is emitted; on the other hand, as Meitner shows, these lines do come definitely from the L, M and N levels under the action of a radiation of energy about $0 \cdot 914 \times 10^5$ volts. It is perfectly straightforward to see in this a γ-ray emitted from the nucleus, like all the other cases, and it is a mere coincidence that its energy happens to be near that of the Kα radiations.

In a subsequent paper Hahn and Meitner* show that it is really uranium X_1 that emits this radiation, and they also find the absorption coefficient with a view to testing whether it is really the K radiation. Absorption experiments can never do more than establish the general region in which lies the frequency of the radiation, and therefore it was quite impossible to settle whether it was actually the K radiation that was emitted or merely a radiation of this general hardness.

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* Hahn and Meitner, 'Zeit. f. Physik,' vol. 17, p. 157 (1923).

As far as we can see, uranium X_1 appears to be a perfectly normal β-ray body, emitting a soft γ-ray from the nucleus like radium D.

The diffuse band, as Meitner states, probably consists of the disintegration electrons, and we now see that it constitutes a very good example of the varying velocity which these electrons always appear to possess once they are outside of the atom. As there is no evidence of the excitation of the K spectrum, we have to assume these electrons leave the nucleus with different velocities. This phrase "leaving the nucleus" introduces difficulties. It is clear that the electron before it leaves the nucleus is in a quantitised state, with definite energy, but once outside the atom its energy is found to vary over a considerable range. We have seen that there is no evidence that any inhomogeneity is introduced in passing through the K ring and out to the surface, and so the actual observed inhomogeneity must be effected before this. Whether this is called in the nucleus or not is at the moment immaterial. There must be very intense electric fields associated with the nucleus and the inhomogeneity could well be due, as Rosseland* has suggested, to the emission of general γ-radiation, resulting from the violent acceleration of the electron.

The close study of the radium B and C β-ray spectrum has not only confirmed the general origin of the lines, but in addition has brought out some very interesting facts. We have found curious inversions in the relative strength of the lines from the various L levels in different parts of the spectrum. Again, there is evidence that while most of the radium B γ-rays are emitted before the disintegration in the case of one γ-ray it is simplest to assume that it is emitted afterwards.

At the moment the evidence is insufficient to justify any attempt to give a theory of the β-ray disintegration, but on the other hand it is possible to separate the various phenomena and to put them provisionally into general relation with each other.

The two fundamental events in the disintegration are the emission of the γ-rays and the emission of the disintegration electron. We have seen that it appears simplest to consider these two events as being associated with two different systems, between which there is some coupling such that the exact instant of the emission of the disintegration electron is connected with the occupation of certain stationary states of the γ-ray level system. Further, the ejection of the disintegration electron alters the energy of these particular stationary states to approximately the same extent. The cause of the final distribution of velocity of the disintegration electrons is possibly due to the emission of continuous γ-rays, but it is an independent problem on which at the moment there is no evidence. The same may almost be said of the closer description of the γ-ray stationary states, except that we have brought evidence in favour of the view that the stationary states of the radium C nucleus are similar in structure to those of radium B, but with slightly increased energies. If this can be substantiated, it should be of the greatest importance in obtaining a closer idea of the system occupying these states.

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* Rosseland, 'Zeit. f. Physik,' vol. 14, p. 173 (1923).

We are greatly indebted to Professor Sir Ernest Rutherford for his advice and help in the discussion of the problems treated in this paper.

Summary.

1. The new measurements of the frequencies of the γ-rays have confirmed strongly the conclusion that the γ-rays are due to transitions between the stationary states in the nucleus.

2. Diagrams of the probable nuclear levels of radium B and radium C are given. These two sets of levels show striking similarities, which fact is considered to be of great importance.

3. The change in the relative absorbing powers of the L sub-groups described in the previous paper is discussed and shown to be consistent with the results of Robinson.

On the Velocity of Sound in Gases and Vapours, and the Ratio of the Specific Heats.

By HAROLD B. DIXON, C.B.E., D.Sc., F.R.S., and GILBERT GREENWOOD, M.Sc.

(Received December 6, 1923.)

The experiments described in this memoir were made in continuation of those carried out by Dixon, Campbell and Parker on the velocity of sound in gases at high temperatures.[*] Our object was to determine the velocity of sound in the vapours of the low-boiling inflammable liquids ether, methyl and ethyl alcohols, pentane, hexane and benzene, and in condensable gases such as ethylene and ammonia.

Corrigendum.

As a preliminary we desire to take this opportunity of making a correction (which Prof. J. R. Partington has pointed out to us) in the calculation of the ratio of the specific heats from the velocity of sound in "free" nitrogen, carbon dioxide, methane and ethane, given in the former paper. For instance, by the use of round figures, the values of γ between 0° and 500° C. derived from the velocity of sound in free nitrogen were made 0·002 too high, a difference which appreciably affects the value of C_v calculated from it; and similarly the values of γ for carbon dioxide between 0° and 300° C. were made too low. The Tables XI, XIII, XIV and XV printed on pages 23 and 24 of that memoir have therefore been recalculated, the new gas constant R = 1·9875 being used, and should read as follows:—

Corrected Table XI.—Nitrogen.

$M = 28 \cdot 02$ $\qquad p_c = 33$ At. $\qquad T_c = 126° \cdot 5$ Abs.

Temp. C.	$C_p - C_v$.	C_p/C_v.	C_v.	C_v calculated from $4 \cdot 81 + 0 \cdot 00041$ T.
°				
0	1·9976	1·406	4·921	4·922
100	1·9915	1·4015	4·960	4·963
200	1·9894	1·397	5·011	5·004
300	1·9886	1·394	5·047	5·045
400	1·9882	1·3905	5·091	5·086
500	1·9879	1·3875	5·130	5·127
600	1·9878	1·385	5·163	5·168
700	1·9877	1·382	5·203	5·209
800	1·9877	1·379	5·245	5·250
900	1·9876	1·376	5·286	5·291
1,000	1·9876	1·373	5·329	5·332

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[*] 'Roy. Soc. Proc.,' A, vol. 100 (1921).

Corrected Table XIII.—Carbon Dioxide.

M = 44·005 p_x = 73 At. T_x = 304° Abs.

Temp. C.	$C_p - C_v$.	C_p/C_v.	C_v.	C_v calculated from 5·9 + 0·0031 T.
°				
0	2·0509	1·310	6·616	6·746
100	2·0124	1·2855	7·049	7·056
200	1·9997	1·2715	7·365	7·366
300	1·9944	1·2595	7·685	7·676
400	1·9917	1·249	8·000	7·986
500	1·9903	1·240	8·293	8·296
600	1·9894	1·2313	8·601	8·606

Corrected Table XIV.—Methane.

M = 16·037 p_x = 50 At. T_x = 177·5° Abs.

Temp. C.	$C_p - C_v$.	C_p/C_v.	C_v.	C_v calculated from 6·92 + 0·0183 T.
°				
0	2·0059	1·304	6·598	6·92
100	1·9947	1·228	8·749	8·75
200	1·9910	1·188	10·590	10·58
300	1·9895	1·160	12·434	12·41
400	1·9887	1·139	14·307	14·23
500	1·9883	1·124	16·032	16·06
600	1·9881	1·111	17·911	17·90

Corrected Table XV.—Ethane.

M = 30·058 p_x = 50·2 At. T_x = 307° Abs.

Temp. C.	$C_p - C_v$.	C_p/C_v.	C_v.	C_v calculated from 87·5 + 0·019 T.
°				
10	2·0727	1·231	8·97	8·94
50	2·0448	1·213	9·60	9·70
100	2·0247	1·190	10·66	10·65

The Velocity of Sound in Gases and Vapours measured directly in a Lead Tube.

The method of timing the passage of a sound-wave between the two ends of a coiled pipe, and of eliminating errors of the chronograph, was the same as that published in the 'Proceedings' two years ago.

The tube A for containing the gases or vapours was a leaden pipe of 25 mm. internal diameter coiled round an iron drum and immersed in a large water-bath B. The two ends of the lead coil were joined to the aluminium end-pieces C previously described, but whereas in the former experiments the end-pieces were kept cool by a stream of water, in the present experiments with vapours they were kept hot by a current of steam passing through the jackets. With regard to the two small lengths of pipe, emerging from the water of the bath and joined to the end-pieces, it was assumed that half their length was at the temperature of the bath and half at the temperature of the end-pieces. The junctions were made as close as possible to the lid of the bath, through holes in which the tube passed, and the small intermediate lengths of tube were jacketed with cotton-wool. The water was kept well stirred by air blown through a perforated ring at the bottom of the bath.

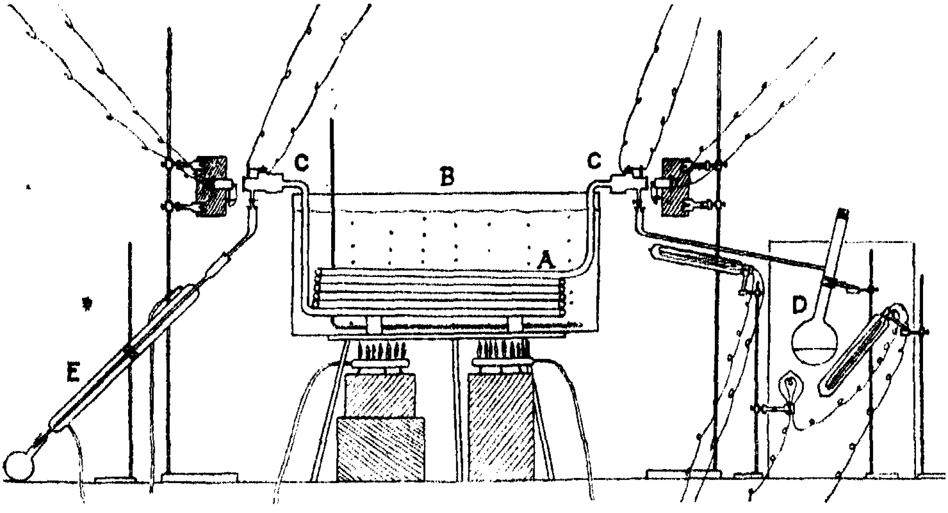

Fig. 1.—Arrangement of Lead Coil in Water-bath.

It was found that the interior of the end-pieces was maintained almost constantly at 99° C. The total distance travelled by the sound wave between the electric "breaks"—measured along the axis of the coiled tube at 15° C.—was 12·37 m.; the distance travelled at the bath temperature was 11·95 m., and the distance travelled at the end-piece temperature was 0·42 m.

To correct the chronograph readings for the rate of the pendulum over different lengths of arc, for the expansion of the lead pipe and for the higher temperature of the end-pieces, the following formula was used :—

$$V = \frac{100F}{L\sqrt{372}}\left[11 \cdot 95 \{1 + 0 \cdot 000028 (t - 15)\} \sqrt{372} + 0 \cdot 42 \sqrt{T}\right]$$

where F is the mean length of the chord of the arc traversed by the pendulum in 0·01 second, L is the total length of the chord between the break-marks on the chronograph plate, 0·000028 is the co-efficient of linear expansion of lead, and t and T are the temperatures of the bath on the centigrade and the absolute scales.

Velocity of Sound in Air.

The first determinations were made with air in the tube at different temperatures between 20° C. and 90° C. As an illustration of the readings obtained we give below the individual lengths of the chords of the arcs traced by the style on the pendulum-plate during the passage of the sound-wave from one break to the other in dry air at 20° C. In the readings under A and A_1 the sound was sent in one direction through the tube, in those under B and B_1 the sound was sent in the other direction ; between A and A_1, and between B and B_1 the chronograph connexions were reversed—in order to eliminate any errors of the electro-magnets. The mean of each group of four readings was taken as one measurement.

Table I.—Dry Air, at 20° C.

A.	B.	A_1.	B_1.	Mean mm.
92·1	93·5	93·7	92·0	92·82
92·7	92·5	92·6	92·8	92·65
92·9	92·5	92·7	92·9	92·75
92·9	93·0	92·6	92·9	92·85
92·8	92·8	92·9	92·6	92·78
93·0	92·6	92·7	92·6	92·72
93·2	92·8	92·4	92·8	92·80
92·9	92·6	92·4	92·9	92·70
92·7	92·8	93·2	92·6	92·82
92·5	92·9	92·8	92·6	92·70

F = 25·55 mm. Average = 92·76 mm.

The velocity of sound calculated from this figure is **339·5 m.p.s.**, the mean length of the chord of the arc traversed by the style on the plate in 0·01 second being 25·55 mm.

In a similar manner the velocity of sound in dry air was determined at different temperatures and the following *mean* chronograph measurements were obtained by taking the average of the four readings :—

Table II.—Dry Air.

At 42°.	49°.	62°.	65°.	77°.	80°.	86°.	90°.
89·48	88·55	86·88	86·49	84·85	84·70	84·25	83·72
89·42	88·45	86·73	86·38	85·00	84·75	84·18	83·62
89·40	88·48	86·60	86·48	84·88	84·62	84·25	83·60
89·40	88·48	86·92	86·50	85·18	84·75	84·10	83·70
89·38	88·45	86·72	86·55	85·18	84·82	83·92	83·60
89·45	88·45	86·65	86·49	85·05	84·70	84·00	83·62
89·40		86·95	86·36	85·12	84·70	83·98	83·58
		87·00	86·43	84·88	84·65	83·92	83·78
		87·00		85·12	84·78		83·65
				85·10	84·75		83·50
Average— 89·42	88·48	86·83	86·46	85·04	84·72	84·07	83·64 mm.
F = 25·56	25·56	25·57	25·571	25·575	25·576	25·578	25·579mm
Velocity— 352·9	356·8	364·1	365·8	372·3	373·9	376·9	378·9 mm.

From these measurements a graph was drawn which was used to confirm the values found in the later experiments.

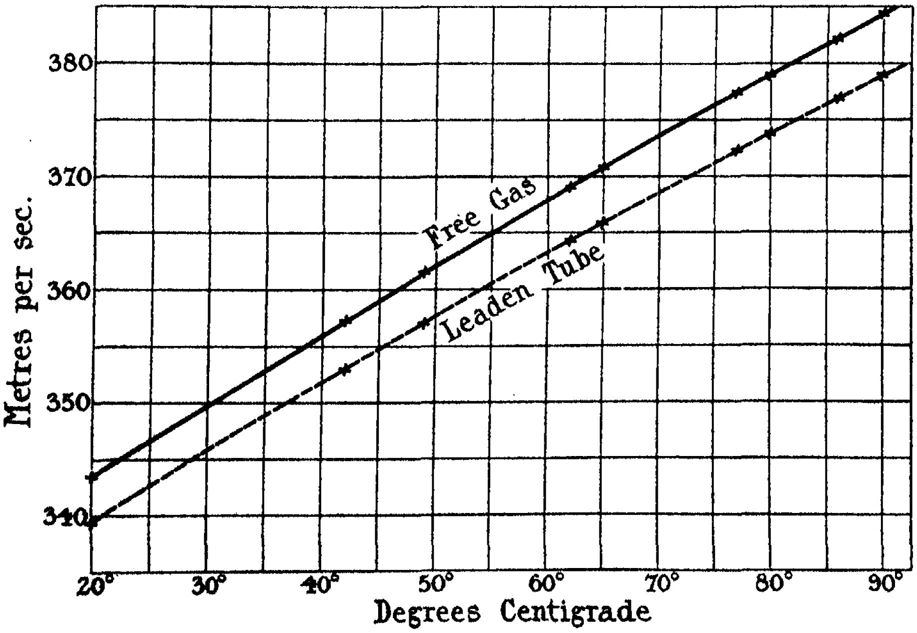

FIG. 2.—Velocity of sound in air.

Velocity of Sound in Vapours.

In carrying out an experiment, determinations were first done in dry air free from carbon dioxide. Air was introduced through the side-tube and tap in the end-piece and allowed to pass slowly through the coil all the time. When the temperature of the bath was correct a set of four readings was obtained and the mean taken. Several such means in close agreement with the value on the air graph were required before the apparatus was considered as working correctly. When this state had been attained the vapour was *introduced. To do this, the purified liquid was put, together with a few pieces of porcelain, into a distilling flask D, to the side-tube of which an adapter had* been fused. This was fitted on to the side-tube of one of the end-pieces, whilst to the other end-piece was fitted a Liebig condenser E and a receiver. The distilling flask itself fitted inside an asbestos air-bath heated by electric heating lamps; there was another lamp under the side-tube of the flask to prevent condensation of the vapour on its way to the experimental coil. The liquid was boiled vigorously until it was distilling quickly into the receiver; the rate of boiling was then decreased, but vapour was kept passing through the apparatus all the time determinations were in progress. If the coil had been filled with vapour when the determinations began, the values remained consistent; if not, the first few variable values were ignored.

Table III.—Ether Vapour at 44° C.

I.	II.	III.	IV.	Mean.
165·2	166·2	166·6	165·1	165·78
166·1	166·1	166·1	166·1	166·10
165·4	166·4	165·4	165·5	165·68
166·0	166·0	166·2	166·0	166·05
165·6	165·6	165·8	165·6	165·65
165·6	166·7	166·7	165·6	166·15

F = 25·305 mm.

Average = 165·90

The velocity calculated from this figure is **184·4 m.p.s.**

Table IV.—Ether Vapour at 49° C.

I.	II.	III.	IV.	Mean.
163·8	164·7	164·9	163·8	164·30
164·1	164·1	164·4	163·9	164·12
164·4	164·5	164·3	164·4	164·40
164·2	164·0	164·3	164·2	164·18
163·9	164·7	164·7	164·2	164·38
164·2	164·5	164·6	164·0	164·32

F = 25·313 Average = 164·29

The velocity calculated from this figure is **190·3 m.p.s.**

Table V.—Ether Vapour at 66° C.

I.	II.	III.	IV.	Mean.
159·5	159·5	159·3	158·9	159·30
159·1	159·1	159·1	158·4	158·92
158·7	159·3	159·4	158·2	158·90
159·8	158·6	158·2	158·8	158·85
159·5	159·6	159·1	158·9	159·22

F = 25·334 mm. Average = 159·04

The velocity calculated from this figure is **196·9 m.p.s.**

Table VI.—Ether Vapour at 80° C.

I.	II.	III.	IV.	Mean.
155·3	156·5	156·5	155·3	155·90
155·8	155·7	155·7	155·8	155·75
155·0	155·7	155·7	155·2	155·40
155·6	155·2	155·3	155·6	155·42
155·4	155·5	155·9	155·5	155·58
154·7	156·1	156·1	155·1	155·50

F = 25·348 mm. Average = 155·59

The velocity calculated from this figure is **201·8 m.p.s.**

Table VII.—Pentane Vapour at 43° C.

I.	II.	III.	IV.	Mean.
163·9	164·4	164·2	163·7	164·05
163·9	163·6	163·5	163·7	163·68
164·6	163·3	163·5	163·8	163·80
163·4	164·0	163·5	163·2	163·52
164·0	163·8	163·6	163·5	163·72
164·0	163·1	163·3	164·2	163·65

F = 25·315 mm. Average = 163·74

The velocity calculated from this figure is **190·85 m.p.s.**

Table VIII.—Pentane Vapour at 63° C.

I.	II.	III.	IV.	Mean.
157·8	159·0	159·0	157·7	158·38
157·7	157·8	157·3	157·3	157·52
157·9	157·2	157·0	157·9	157·50
156·7	157·4	157·1	156·2	156·85
156·7	156·9	156·5	156·6	156·68
157·2	156·6	156·5	156·5	156·70
156·7	157·0	156·7	156·2	156·72

F = 25·34 mm. Average = 157·19

The velocity calculated from this figure is **199·45 m.p.s.**

Table IX.—Pentane Vapour at 77° C.

I.	II.	III.	IV.	Mean.
153·6	154·8	154·2	154·0	154·15
152·9	156·0	154·9	153·6	154·35
153·2	155·0	154·2	153·7	154·05
153·2	154·8	153·5	153·6	153·78
153·8	154·2	154·7	153·4	154·05
154·7	154·7	153·9	153·0	154·08
153·8	154·5	154·3	153·0	153·90

F = 25·355 mm. Average = 154·05

The velocity calculated from this figure is **203·75 m.p.s.**

Table X.—Pentane Vapour at 86° C.

I.	II.	III.	IV.	Mean.
153·2	152·2	153·4	151·8	152·65
152·6	152·0	153·2	151·8	152·40
152·4	152·1	152·7	151·3	152·12
152·5	152·8	153·3	151·0	153·32
153·0	152·4	153·2	151·9	152·62

F = 25·36 mm. Average = 152·42

The velocity calculated from this figure is **206·1 m.p.s.**

Table XI.—Ethyl Alcohol Vapour at 90° C.

I.	II.	III.	IV.	Mean.
118·3	119·0	118·6	118·3	118·55
118·0	118·9	118·9	118·0	118·45
118·6	119·4	118·8	119·0	118·95
118·8	118·0	118·2	118·7	118·42
119·1	118·6	118·3	118·9	118·72
118·0	119·9	119·9	118·0	118·85
118·6	118·0	118·0	118·7	118·42
118·6	118·5	118·4	118·7	118·55
118·4	119·5	119·2	118·6	118·92

F = 25·48 mm. Average = 118·65

The velocity calculated from this figure is **266 m.p.s.**

Table XII.—Methyl Alcohol Vapour at 77° C.

I.	II.	III.	IV.	Mean.
98·0	98·0	97·8	97·2	97·75
98·0	98·0	97·6	97·5	97·78
97·0	97·2	98·2	97·2	97·40
98·0	97·9	98·6	97·4	97·98
97·8*	97·9	98·9	97·7	98·05
99·0*	97·9	97·9	97·0	97·95
98·3*	98·3	98·7	98·1	98·33

F = 25·54 mm. Average = 97·90

In the three experiments marked * the second sample of alcohol was used. The velocity calculated from the average figure is **322·8 m.p.s.**

Table XIII.—Benzene Vapour at 90° C.

I.	II.	III.	IV.	Mean.
158·0	157·0	158·0	157·6	157·65
158·0	157·6	158·6	157·4	157·90
157·7	157·9	158·6	157·2	157·85
157·3	157·7	157·8	156·3	157·28
157·4	157·0	157·2	157·0	157·30
157·5	157·3	157·2	157·9	157·47
158·0	157·1	157·3	158·4	157·70
157·0	157·5	157·6	157·2	157·32
158·3	157·3	157·1	157·7	157·60
157·0	156·7	157·8	157·1	157·40
156·1	159·1	159·1	156·5	157·70

F = 25·34 mm. Average = 157·56

The velocity calculated from this figure is **199·25 m.p.s.**

Table XIV.—Hexane Vapour at 80° C.

I.	II.	III.	IV.	Mean.
169·1	169·6	170·2	169·7	169·65
170·3	169·3	168·9	170·1	169·65
169·9	170·3	171·3	169·0	170·12
170·3	169·9	170·2	170·4	170·20
170·1	169·6	170·6	169·8	170·03
170·3	169·7	170·2	169·7	169·98
170·1	169·2	170·2	169·4	169·72
170·4	169·7	170·6	170·1	170·20
170·2	171·0	171·2	169·7	170·28

F = 25·285 mm. Average = 169·98

The velocity calculated from this figure is **184·2 m.p.s.**

Table XV.—Ammonia at 16·5° C.

I.	II.	III.	IV.	Mean.
74·3	74·6	74·3	74·9	74·50
73·8	75·0	74·5	75·2	74·62
74·0	74·6	74·4	74·6	74·40
74·1	74·0	74·4	75·1	74·40
74·0	74·8	74·5	74·3	74·40
74·6	74·2	74·1	75·5	74·60

F = 25·50 mm. Average = 74·49

Velocity at 16·5° C. = **423·4 m.p.s.**

Table XVI.—Ammonia at 41° C.

I.	II.	III.	IV.	Mean.
71·5	72·1	72·2	71·6	71·85
71·1	71·8	72·0	72·1	71·75
72·6	71·2	72·4	72·3	72·12
69·9	72·6	72·3	71·3	71·52
71·7	71·2	72·3	71·8	71·75
70·8	71·5	72·3	70·8	71·35

F = 25·60 mm. Average = 71·73

Velocity at 41° C. = **440·8 m.p.s.**

Table XVII.—Ammonia at 63·5° C.

I.	II.	III.	IV.	Mean.
68·6	71·1	69·4	69·9	69·50
69·1	70·0	69·7	69·4	69·55
68·9	70·1	69·8	68·9	69·42
70·0	69·0	69·8	69·2	69·50
68·6	69·6	70·6	69·4	69·55
69·2	69·1	69·8	69·4	69·38
68·9	69·9	69·8	68·3	69·22
69·5	68·4	70·8	69·5	69·55
68·7	69·0	70·1	69·5	69·32
68·8	69·8	70·0	69·6	69·55
69·4	69·6	70·1	69·0	69·52

F = 25·61 mm. Average = 69·46

Velocity at 63·5° C. = **455·9 m.p.s.**

Table XVIII.—Ammonia at 86° C.

I.	II.	III.	IV.	Mean.
67·7	66·7	67·6	68·2	67·55
66·8	67·8	68·4	66·7	67·42
68·0	67·8	67·9	66·9	67·65
66·8	67·6	68·0	66·9	67·32
68·0	66·8	67·6	68·4	67·70
67·0	67·2	68·6	66·7	67·38
67·9	66·6	67·7	66·9	67·28
67·0	66·9	68·7	67·5	67·52

F = 25·62 mm. Average = 67·48

Velocity at 86° C. = **470·2 m.p.s.**

Table XIX.—Ethylene at 12° C.

I.	II.	III.	IV.	Mean.
98·8	97·7	98·3	98·0	98·20
98·9	97·7	98·0	97·5	98·02
99·3	97·8	98·2	98·2	98·38
98·1	97·6	97·8	98·0	97·88
98·2	98·0	97·9	97·6	97·92
98·4	98·2	99·0	97·3	98·22
98·6	97·6	97·3	98·3	97·98
98·4	97·9	98·0	97·9	98·05

F = 25·536 mm. Average = 98·08

Velocity at 12° C. = **320·7 m.p.s.**

Table XX.—Ethylene at 41·5° C.

I.	II.	III.	IV.	Mean.
94·4	93·6	93·7	94·4	94·02
92·4	94·6	94·8	94·0	93·95
93·1	95·0	94·1	94·8	94·25
93·3	94·0	94·5	94·0	93·95
94·1	93·5	93·8	95·8	94·30
94·2	93·8	92·5	95·1	93·90
94·4	93·7	94·1	94·4	94·15

F = 25·548 mm. Average = 94·07

Velocity at 41·5° C. = **335·4 m.p.s.**

Table XXI.—Ethylene at 89° C.

I.	II.	III.	IV.	Mean.
88·6	89·1	88·7	87·7	88·52
88·0	89·1	88·4	87·7	88·30
88·3	88·6	88·8	88·7	88·60
88·3	89·0	89·4	88·1	88·70
88·9	88·1	89·0	88·2	88·55
88·6	87·6	89·2	87·9	88·32
88·3	88·1	88·9	88·4	88·42
88·9	88·1	88·5	88·3	88·45

F = 25·565 mm. Average = 88·48

Velocity at 89° C. = **358·0 m.p.s.**

The next experiments with ethylene at 63·5° were made in a shorter coil, of which 11·91 m. were at bath temperature and 0·37 m. at 99°.

Table XXII.—Ethylene at 63·5° C.

I.	II.	III.	IV.	Mean.
89·5	90·5	89·2	89·3	89·62
88·6	90·3	90·6	88·6	89·52
89·4	89·8	89·6	89·2	89·50
89·2	90·8	90·1	88·4	89·62
89·7	90·7	89·6	89·3	89·82
88·8	90·1	90·2	89·4	89·62
89·4	89·9	89·7	89·5	89·63
90·0	89·1	89·5	89·3	89·48
89·9	89·5	89·9	88·8	89·52

F = 25·17 mm. Average = 89·59

Velocity at 63·5° C. = **345·0 m.p.s.**

The Velocity of Sound in free Gases and Vapours.

In making the correction from the data obtained in the lead coil for the velocity of sound in the "free" gases and vapours we have adopted the formula given by Prof. S. Chapman* for the coefficient of conductivity

$$k = f\eta C_v$$

where f is a function of the number of atoms in the molecule. Pollock† has shown by use of the data of Eucken‡ that this function can be represented by—

$$f = \frac{7\cdot 32\,(\gamma - 1)}{\gamma^{1\cdot 3}}.$$

Hence making the substitutions in the final expression for c, we have

$$c = \sqrt{\frac{\eta_0\,T^{\frac{3}{2}}\,(273 + C_1)}{\rho_0\,273^{\frac{3}{2}}\,(T + C_1)}}\left[1 + \sqrt{732}\,\frac{(\gamma - 1)^{\frac{3}{2}}}{\gamma^{1\cdot 15}}\right].$$

Velocity of Sound in Free Air and Evaluation of the Constant K.

In the calculation of the Kirchhoff constants, the following values were used:—

$\gamma = 1\cdot 41.$

$\rho_0 = 1\cdot 2928 \times 10^{-3}.$

$\eta_0 = 1\cdot 733 \times 10^{-4} : C_1 = 119\cdot 4.$

These figures give the value of the Kirchhoff constant at 20° C. to be $c_{20} = 0\cdot 576$.

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* 'Phil. Trans.,' A, vol. 216, p. 279 (1916).

† 'J. Roy. Soc., N.S.W.,' vol. 49, p. 249 (1915).

‡ 'Phys. Zeit.,' vol. 14, p. 324 (1913).

The velocity in the tube V^1 at 20° C. is 339·5 m.p.s.

A value for the velocity in the free gas V at 20° C. was found by Dixon, Campbell and Parker to be 343·55 m.p.s. This gives

$$K = \frac{343 \cdot 55 - 339 \cdot 5}{0 \cdot 576 \times 343 \cdot 55} = 0 \cdot 02.$$

The following table gives the values of the Kirchhoff constants for the various temperatures and the velocities of sound in the free gas, obtained by dividing the velocities in the tube by 1-K*c*. The velocities of sound through air in the tube and in free air at various temperatures are also represented on the graph (fig. 2, page 203).

Table XXIII.

Temp.	*c*.	V in free air.	Temp. ° C.	*c*.	V in free air.
° C.		m.p.s.	°		m.p.s.
20	0·576	*343·55	77	0·674	377·35
42	0·615	357·3	80	0·680	379·0
49	0·627	361·7	86	0·690	382·1
62	0·649	369·1	90	0·696	384·35
65	0·654	370·7			

* This value was assumed in the calculation of K.

Velocity of Sound in Free Ether Vapour.

The approximate value of γ was taken as 1·05. A theoretical value of the density at N.T.P. was obtained by dividing the molecular weight by the ideal molecular volume 22412 c.cs.

This gives $\rho_0 = \dfrac{74 \cdot 08}{22412} = 3 \cdot 3 \times 10^{-3}$.

The data of Rappenecker* on the viscosity of ether vapour were used. He had found the value of C_1 to be 325 and the value of the viscosity at 100° C. to be $9 \cdot 67 \times 10^{-5}$. Hence by Sutherland's equation we get :—

$$\eta_0 = \eta_{100} \cdot \frac{373 + 325}{273 + 325}\left(\frac{273}{373}\right)^{\frac{3}{2}} = 7 \cdot 07 \times 10^{-5}.$$

The following table gives the values of the Kirchhoff constants and the velocities in the free gas.

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* 'Zeit. Phys. Chem.,' vol. 72, p. 695 (1910).

Table XXIV—*Ether.*

Temp.	*c.*	V.	Temp.	*c.*	V.
° C.		m.p.s.	° C.		m.p.s.
44	0·175	189·05	66	0·187	197·65
49	0·178	191·0	80	0·195	202·55

These figures are also represented graphically.

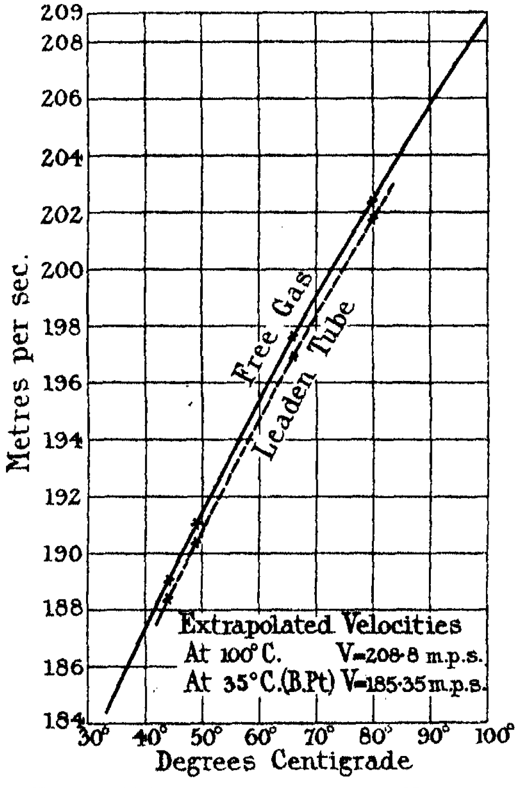

Fig. 3.—Velocity of Sound in Ether Vapour.

Velocity of Sound in Free Ethyl Alcohol Vapour.

The approximate value taken for γ was 1·13. The theoretical value for ρ_0 calculated as in the case of ether was $\rho_0 = 2 \cdot 055 \times 10^{-3}$. Rappenecker's viscosity data were used and the following value obtained for

$$\eta_0 = 7 \cdot 68 \times 10^{-5} : C_1 = 525.$$

The value obtained for the free gas velocity is given below :—

Table XXV—*Ethyl Alcohol.*

Temp.	c.	V.
° C.		m.p.s.
90	0·290	267·55

Velocity of Sound in Free Benzene Vapour.

The approximate value used for γ was 1·09. The theoretical value for ρ_0 is $3 \cdot 48 \times 10^{-3}$. The values for the viscosity obtained from Rappenecker's figures are

$$\eta_0 = 6 \cdot 43 \times 10^{-5} : C_1 = 700.$$

This gives the following velocity as that through the free gas :—

Table XXVI—*Benzene.*

Temp.	c.	V.
° C.		m.p.s.
90	0·198	200·05

Velocity of Sound in Free Pentane Vapour.

The only available viscosity data are those of Rappenecker for iso-pentane. The viscosity of the pentane used will vary only very slightly from this, and so these data may be used in applying the correction. The approximate value taken for γ was 1·07 and the theoretical value for ρ_0 is $3 \cdot 21 \times 10^{-3}$. The viscosity data used were :—

$$\eta_0 = 6 \cdot 25 \times 10^{-5} : C_1 = 500.$$

The corrected values for the velocity through free gas are as follows :—

Table XXVII—*Pentane.*

Temp.	c.	V.	Temp.	c.	V.
° C.		m.p.s.	° C.		m.p.s.
43	0·171	191·5	77	0·190	204·5
63	0·182	200·2	86	0·195	207·05

The graph shows the variation of the velocity of sound in pentane vapour with temperature.

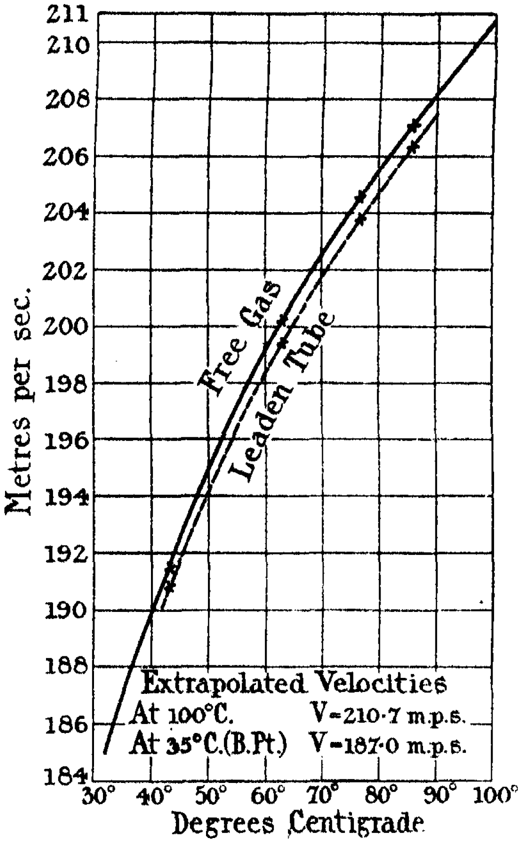

FIG. 4.—Velocity of Sound in Pentane Vapour.

Velocity of Sound in Free Methyl Alcohol Vapour.

The only viscosity determination with methyl alcohol was done by Steudel* who obtained the value :—

$$\eta = 13\cdot5 \times 10^{-5} \text{ at } 66\cdot8^\circ \text{ C.}$$

We may use the simple law of Meyer and v. Obermeyer :—

$$\eta_t = \eta\,(1 + \alpha t).$$

In the case of the vapours of many organic liquids α has the value 0·004. Using this value we find $\eta_{77} = 14\cdot05 \times 10^{-5}$. The calculated value for ρ_{77} is $1\cdot115 \times 10^{-3}$ and the approximate value taken for γ is 1·25. We can now use these data in the simple formula :—

$$c = \sqrt{\frac{\eta}{\rho}}\left[1 + \sqrt{7\cdot32}\,\frac{(\gamma - 1)^{\frac{1}{2}}}{\gamma^{1\cdot15}}\right].$$

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* 'Wied. Ann.,' vol. 16, p. 368 (1882).

We thus find the velocity through the free gas is as follows :—

Table XXVIII—*Methyl Alcohol.*

Temp.	c.	V.
° C.		m.p.s.
77	0·448	325·75

Velocity of Sound in Free Hexane Vapour.

There are no data as to the viscosity of hexane; however, it seems to be a general rule that when a molecule contains a considerable number of atoms, the introduction of several more causes very little change in the viscosity—*cf.* O. E. Meyer.*

Hence the values of η found for iso-pentane were applied to hexane. The approximate value used for γ was 1·05, whilst the theoretical figure for ρ_0 is $3{\cdot}844 \times 10^{-3}$. The corrected velocity and the Kirchhoff constant are given in the following table :—

Table XXIX—*Hexane.*

Temp.	c.	V.
° C.		m.p.s.
80	0·173	184·85

Velocity of Sound in Free Ammonia Gas.

The viscosity data used were those of Vogel and Thomsen. The values obtained at low temperatures are, however, unreliable owing to the enormous amount of absorption which occurs. The values $0{\cdot}943 \times 10^{-4}$ for η_0 and 370 for C_1 were used. Guye's value for $\rho_0 = 0{\cdot}7708 \times 10^{-3}$ was taken. The approximate value of γ was taken as 1·31.

The following table gives the velocities so calculated :—

Table XXX—*Ammonia.*

Temp.	c.	V.	Temp.	c.	V.
° C.		m.p.s.	° C.		m.p.s.
16·5	0·490	427·7	63·5	0·581	461·2
41	0·542	445·5	86	0·621	476·1

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* 'The Kinetic Theory of Gases,' 1899 edition, p. 200.

Velocity of Sound in Free Ethylene.

$\rho_0 = 1 \cdot 2519 \times 10^{-3}$ (Saussure), Graham's value for $\eta_0 = 0 \cdot 966 \times 10^{-4}$ and Sutherland's value for $C_1 = 272$ were used; γ was taken as $1 \cdot 25$.

The values obtained for V are shown below :—

Table XXXI—*Ethylene.*

Temp.	c.	V.	Temp.	c.	V.
° C.		m.p.s.	° C.		m.p.s.
12	0·360	323·0	63·5	0·424	348·0
41·5	0·392	328·1	89	0·439	361·2

Calculation of the Molecular Specific Heats.

The most satisfactory way of calculating γ, the ratio of the two specific heats, would be to substitute an experimental value of the density of the vapour at a temperature at which the velocity of sound has been determined in Laplace's equation and calculate γ directly. Unfortunately this is impossible, owing to the deficiency of data on the densities of unsaturated vapours. Berthelot's equation—

$$\frac{C_p}{C_v} = \frac{V^2 M}{RT}\left[1 - \pi \, . \, \tfrac{9}{64} \, \tau \left(1 - 6\tau^2\right)\right]$$

can be used. Theoretical values for the densities may be calculated, by making use of Van der Waals' equation and the expressions deduced by Guye* for the variation of the "constants" a and b and γ then calculated from these values. If we do this in the case of pentane and ether we find that in both cases the two values of γ calculated by these two methods show satisfactory agreement at the highest temperature, viz., 1·086 and 1·080 for pentane; 1·086 and 1·082 for ether. However, at lower temperatures the equations appear to be more uncertain; the values of γ calculated by the two methods do not agree, and also they are less than the values mentioned above. Hence only the figures deduced from the velocities at the highest temperatures have been regarded as worthy of record. In the case of the other vapours only one determination was possible, and this not very far from the boiling point. The values deduced for these vapours are thus less certain than those for pentane and ether.

The differences of the specific heats $C_p - C_v$ were calculated by the equation

$$C_p - C_v = R\left(1 + \tfrac{27}{16} \pi \tau^3\right).$$

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[*] 'Compt. Rend.,' vol. 140, p. 1242 (1905).

The following table gives the values obtained in this way for γ, C_p and C_v for the vapours investigated—

Table XXXII.

Substance.	Temp.	γ.	$C_p - C_v$.	C_p.	C_v.
	° C.				
Ether	80	1·086	2·202	27·81	25·61
Pentane	86	1·086	2·201	29·50	27·31
Hexane	80	1·080	2·323	31·36	29·03
Ethyl alcohol	90	1·129	2·138	18·72	16·57
Methyl alcohol	77	1·203	2·120	12·56	10·44
Benzene	90	1·097	2·245	25·39	23·15

In the case of ammonia and ethylene the Berthelot equation gave the following values for the specific heats derived from the velocities in the "free" gases :—

Table XXXIII—*Ammonia.*

$M = 17·01$. $p_r = 115·0$. $T_r = 400$.

Temp.	V.	$C_p - C_v$.	C_p/C_v.	C_v.	C_v calculated from $6·525 + 0·002\ t$.
° C.					
16·5	427·7	2·062	1·3144	6·56	6·56
41	445·5	2·045	1·3095	6·61	6·61
63·5	461·2	2·034	1·3062	6·64	6·65
86	476·1	2·025	1·3021	6·70	6·70

Table XXXIV—*Ethylene.*

$M = 28·04$. $p_r = 51·0$. $T_r = 283$.

Temp.	V.	$C_p - C_v$.	C_p/C_v.	C_v.	C_v calculated from $8·06 + 0·0119\ t$.
° C.					
12	323·0	2·0494	1·2502	8·20	8·20
41·5	338·3	2·0327	1·2380	8·54	8·55
63·5	349·1	2·0246	1·2295	8·82	8·82
89	361·2	2·0162	1·2213	9·12	9·12

Purification of the Gases and Vapours.

Air.—The air was freed from moisture and carbon dioxide by passage through a tower of calcium chloride, a tower of soda-lime, followed by a washing bottle of concentrated sulphuric acid.

Benzene.—"Pure" commercial benzene was washed with concentrated sulphuric acid until it gave no further colouration. This removes thiopen. It was then washed with water, followed by strong potash solution. Any traces of carbon disulphide were then removed by washing with a solution of potassium ethylate. It was then washed with large amounts of water and dried with calcium chloride. These last two operations also remove any alcohol left from the potassium ethylate. It was then roughly distilled. The distillate was then dehydrated by metallic sodium and fractionated over sodium. The fraction used boiled 79·9–80·03° C. Its density at 15·0° C. was 0·8830.

Hexane.—This was obtained from a sample specially prepared for us by the Anglo-American Oil Company. It was purified exactly like the benzene (above). After treatment with calcium chloride it was twice fractionated. The fractions near to the boiling point of hexane were then dehydrated by boiling with phosphoric oxide and then distilling from fresh phosphoric oxide. It was then fractionated again. The fraction used boiled at 67·0–68·5° C., and its density at 15·5° C. was 0·6948.

Pentane.—The pentane was purified and fractionated exactly as in the case of hexane. Two different specimens of pentane were used in the experiments; the first from a sample prepared for us by the Anglo-American Oil Co., the second from a sample from Messrs. Capel, Carless & Co. The first, used in the determination at 43° C. boiled at 33·5–35·0° C., and its density at 18·5° C. was 0·6280. The second sample boiled at 35·0–37·0° C., and its density at 16·9° C. was 0·6313. These samples of pentane no doubt contained a mixture of isomers. This fact made itself noticeable by the slight gradual change of the chronograph readings as the distillation of the liquid in the flask proceeded.

Ether.—"Pure" commercial ether was washed with a strong potash solution and then with water; and was dried over calcium chloride. These last two operations also remove alcohol. A rough distillation was then carried out. The distillate was dehydrated over metallic sodium and then over phosphoric oxide. It was then distilled. It boiled at 35·0–35·3° C., and its density at 17·5° C. was 0·7181.

Methyl Alcohol.—"Pure" commercial methyl alcohol was shaken with solid caustic soda, to remove acetic acid and aldehydes. It was then roughly distilled. Any ethyl alcohol was removed by boiling under a reflux for a few hours with a large amount of caustic potash solution and iodine. The methyl alcohol was then distilled off and dehydrated by boiling with quicklime. It was then distilled off the lime and again fractionated. It boiled at 65·1–66·9° C., and had a density of 0·7934 at 21·5° C.

Ethyl Alcohol.—This was treated with solid caustic soda, as in the case of methyl alcohol. It was then roughly distilled. Dehydration was carried out by boiling with metallic calcium under a reflux. It was then fractionated from over more calcium. It boiled at 78·0—78·7° C., and its density at 16·0° C. was 0·7950.

Ammonia.—The ammonia was obtained from a steel cylinder of liquid ammonia. A sample was completely absorbed by a strong sulphuric acid solution. The gas was passed through a saturated solution of ammonia as an indication of the speed. It was then passed through drying-towers of lime.

Ethylene.—The ethylene was obtained by passing the vapour of ethyl alcohol over pumice moistened with phosphoric acid. At about 200° C. the alcohol is dehydrated according to the equation

$$C_2H_5OH = C_2H_4 + H_2O.$$

The alcohol was boiled from a flask heated by a water bath and as it boiled away it was replenished from a tap-funnel. The vapour passed into a long iron tube heated by a furnace to about 200° C. and full of "phosphorised" pumice.

The ethylene was passed through a cooled vessel to condense water, unchanged alcohol and ether, and then through a wash-bottle containing strong sulphuric acid. This removed the residue of the above impurities. The gas was then stored in a gas holder above water until required for use. The ethylene was passed through drying-towers (1) of solid potash, and (2) of calcium chloride and a wash-bottle of sulphuric acid before use. An analysis of the gas showed it to contain 98·5 per cent. pure ethylene, the residue being mainly nitrogen. A certain amount was therefore liquefied, but experiments with the gas so purified gave results not appreciably different from those obtained with the uncondensed gas. This result follows from theoretical considerations. 1 per cent. nitrogen would only affect the velocity by ·04 per cent. The accuracy of the apparatus is only about 0·1 per cent., hence the addition of up to 2 per cent. nitrogen has no appreciable effect.

We desire to thank Mr. A. J. Bradley, M.Sc., for the assistance he has afforded us in carrying out these measurements, and the Scientific and Industrial Research Board for a grant to one of us.

The Absorption Spectra of Mixed Metallic Vapours.

By S. Barratt, B.A. (Oxon.), Dept. of Chemistry, University of Leeds.

(Communicated by Prof. T. R. Merton, F.R.S. Received Jan. 1, 1924.)

[Plate 2.]

It has been known for many years that bands of great complexity occur in the absorption spectra of the alkali metals. The extensive absorption bands of sodium vapour in the green and red portions of the spectrum have, in particular, attracted considerable attention. R. W. Wood has discussed fully the structure of these bands, the manner in which they fluctuate with change in certain physical conditions, and their connection with the fluorescence spectrum.

The existence of these bands leads to the conclusion that a certain number of the atoms in an alkali metal vapour are associated, though other considerations have indicated that the proportion present in the molecular form cannot be large. It is reasonable to suppose that, in a mixture of the vapours of two alkali metals, "mixed" molecules containing atoms of both elements will exist, in addition to those normally present in the unmixed vapours. These "mixed" molecules if present in sufficient number will exhibit an absorption spectrum, probably similar in character to the bands of the simple alkali metals. In the present communication a new band spectrum is described which is developed only in the vapour of mixtures of sodium and potassium and which, it is suggested, is produced by the sodium-potassium molecules present in the mixed vapour.

Previous observations on the spectra of mixed metallic vapours are very few in number. Liveing and Dewar* observed a band or diffuse line in the absorption of mixtures of sodium and magnesium vapours, and a similar phenomenon with potassium and magnesium.

P. V. Bevan† mentions absorptions which he observed only with mixtures of rubidium with sodium and of caesium with sodium. The present experiments with sodium and potassium were designed as the beginning of a more complete study of this class of spectra.

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* 'Roy. Soc. Proc.,' A, vol. 27, p. 350 (1878), and 'Collected Papers,' p. 13.

† 'Roy. Soc. Proc.,' A, vol. 83, p. 421 (1910).

Experimental.

The absorbing column of metallic vapour was maintained in a steel tube heated electrically by a coil of nichrome ribbon. The heated portion of the tube, about a foot in length, was surrounded by a thick layer of magnesia. A brass flange was soldered to each end of the tube, and a brass plate with a quartz window was screwed to each flange. These joints were made gas-tight by rubber washers greased with tap-grease. They proved as effective for their purpose as the usual wax joint, and were opened and sealed with much greater readiness. The ends of the tube were water-cooled by small coils of copper tubing soldered to the steel. The apparatus was evacuated through a side-tube by a Pfeiffer rotary oil pump, but to prevent too rapid distillation of the metals in most of the experiments the tube was filled with hydrogen at atmospheric pressure from a Kipps apparatus. The life of the furnace tube was prolonged by using an inner iron sheath to prevent contact of the vapour with the heated portion. This sheath was removed at the end of an experiment to be cleaned and recharged. The source of the continuous background was the positive crater of a carbon arc consuming about 8 amps.

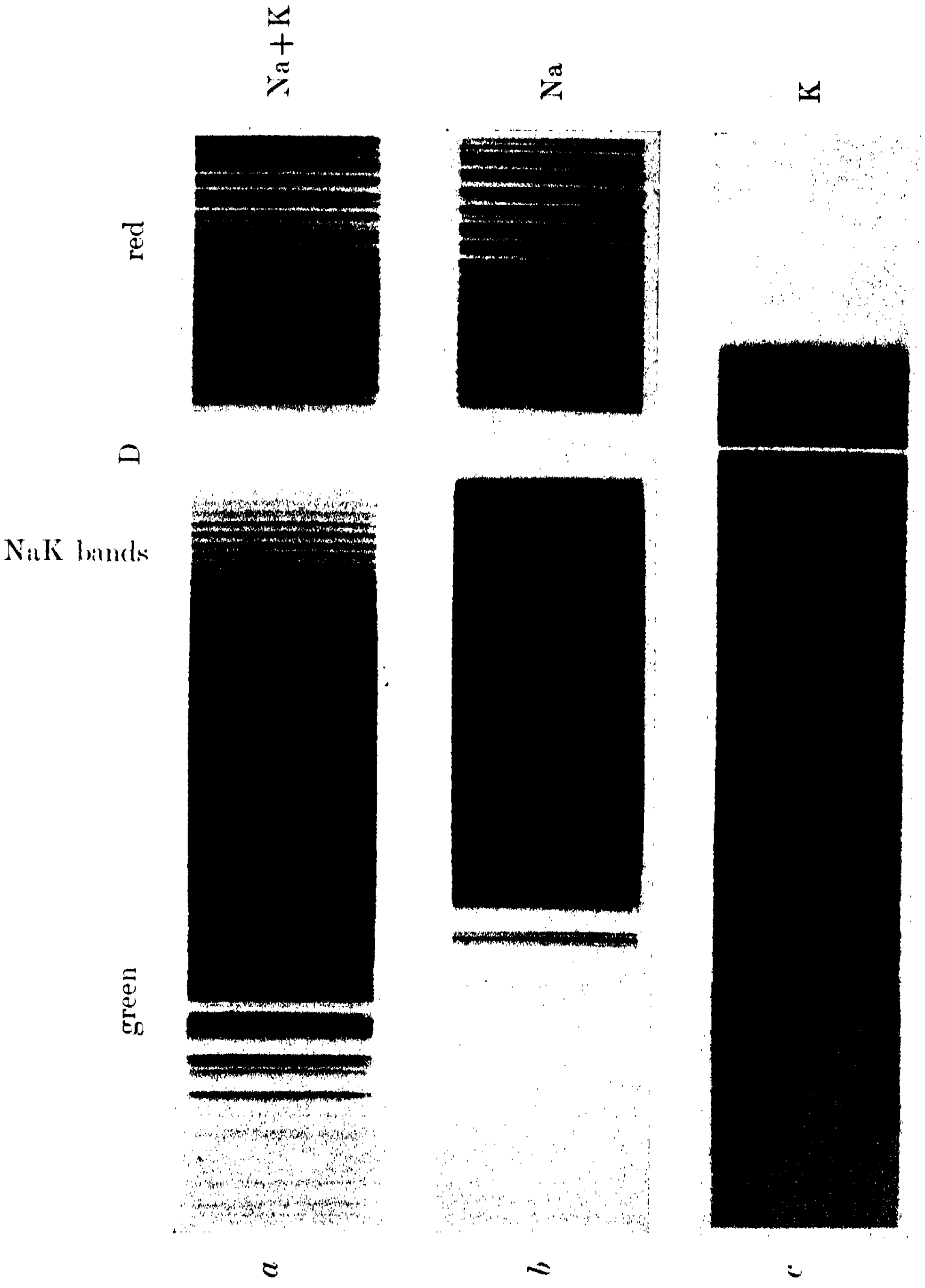
The spectra were photographed on a Hilger constant deviation instrument.

Absorption of Sodium-Potassium Mixtures.

The visible absorption of rare sodium vapour is limited to the D lines. As the density of the vapour increases the banded absorption appears, first in the blue-green and then in the red. At greater densities only a narrow region in the green and part of the violet are transmitted. Potassium vapour has an absorption band in the red and a weaker one in the blue.

On heating a mixture of roughly equal quantities of the two metals in the furnace tube, a new band absorption was observed in the yellow, reaching from the red side of the widened D lines to about λ 5650. This spectrum and the strongest of the red sodium bands require roughly the same density of sodium vapour for their development. This density is far below that at which either sodium or potassium, taken singly, exhibits absorption in the same region as the new bands.

The appearance of the absorption of the mixed vapours is shown in spectrum (*a*) of the plate. (*b*) and (*c*) are comparison photographs of the absorptions of sodium and potassium vapours respectively taken through vapours of greater density than that which was used in obtaining (*a*). The density of the potassium vapour was too great to show the structure of the red band, which appears as a continuous absorption. Sufficient sodium was present in the potassium to


Na+K
Na
K
red
D
NaK bands
green
a
b
c

give a narrow D-line absorption, and the rubidium lines λλ 4216 and 4202 could also be detected on the plates.*

The new sodium-potassium absorption comprises a series of bands degraded towards the red and spaced at intervals of about 20 A. Each band consists of fine lines, separated in the middle of the band by intervals of a few Angstrom units, but much more closely packed near the head. With the dispersion available (only 70 A per millimetre in this region) the individual lines were too close to be measured, or to appear distinctly in the reproduction, but the wave-lengths of the heads of the bands have been determined and are as follows :—

Wave-lengths of Heads in the Sodium-Potassium Spectrum.

5955·0
5931·8
(D line absorption)
5867·0
5846·0
5824·6
5803·7
5783·5
5764·3
5746·1
5728·6
5712·1
5696·0
5680·9
5667·4
5654·1
5645·2

The broadened D line absorption unfortunately prevents the observation of the complete spectrum, as even on photographs taken with the lowest density vapour that was practicable, the wave-length range obscured by the D lines includes the probable positions of two heads. The wave-lengths given are the means of values obtained from two plates, on which the lines of the iron arc were photographed in juxtaposition to the bands, and were used as standards. The lines at the head of the bands were not resolved, a fact which interfered considerably with the accuracy of the measurements. The agreement among individual estimates was good, but this is a small indication, in such a case, of the accuracy attained. The heads are arranged at least approximately according to the usual Deslandres law; but experiments with a greater dispersion would be necessary for the adequate discussion of this point.

The intensity of the absorption diminishes markedly at the short wave-length end of the group of bands. Alteration of the gas pressure in the furnace tube from hydrogen at atmospheric pressure down to the vacuum obtained with a rotary oil pump had no appreciable influence on the appearance of the bands.

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* I have been unable to find any previous reference to the continuous absorption which appears with fairly dense potassium vapour. This is shown on the plate, and has, in fact, been slightly exaggerated in the process of reproduction. It extends from the short wave length limit of the observations to the diffuse line or band absorption at λ5770, where it ends abruptly.

It has been suggested that the molecules responsible for certain band spectra are formed by the combination of normal atoms with those "activated" by absorption of radiation corresponding to the principal series lines. It is known that the molecules which give rise to the band spectrum of sodium are not of this type, and the same conclusion has now been reached for these sodium-potassium bands. A mixture of the vapours of the two metals was illuminated by light from the arc, cut down by a combination of filters to a narrow spectral region in the green, which did not include light of the same wave-length as the D lines. The small portion of the new bands which was included in the transmission range was present in its usual intensity. It is therefore clear that the principal series absorption has no connection with the production of this spectrum.

Absorption of Magnesium Vapour.

It is intended to extend these observations on mixed vapours to include several other metals in addition to the alkalis. Preliminary experiments have already been attempted with mixtures containing magnesium; but the temperature required to produce a sufficient density of magnesium vapour can barely be reached with the furnace described above. It is of interest, however, that during these experiments λ 4571 was consistently observed in absorption.

According to the quantum theory of line absorption spectra, the unexcited vapour of the metals of Group 2 of the periodic table should absorb the lines of those series which converge to the limit 1S. The important line $1S-2p_2$, which forms the "single line spectrum" of these metals when their vapours are excited by low-voltage electrons, has already been observed in absorption for all the elements of this group except magnesium. McLennan* was not able to detect the absorption of λ 4571, the magnesium line in question in a column of rare vapour. In all the present experiments, however, a very definite absorption of this line was obtained. The presence of hydrogen made the observation of the absorption possible at lower temperatures, but the gas was not essential for its appearance. The furnace tube in McLennan's experiments was heated by coal-gas, but otherwise the apparatus was very similar to that described above, and it is difficult to see what circumstance led to the conflicting result.

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* 'Roy. Soc. Proc.,' A, vol. 92, p. 574 (1916), and see also Foote and Mohler, 'The Origin of Spectra,' p. 84.

The author is greatly indebted to Prof. Merton for the suggestion of this field of research. The Hilger spectrograph was purchased with a grant from the Royal Society.

The Ratio of the Specific Heats of Nitrogen and of Oxygen.

By J. R. PARTINGTON, D.Sc., and A. B. HOWE, M.Sc.

(Communicated by Prof. H. B. Dixon, F.R.S. Received December 6, 1923.)

The investigation of the ratio of the specific heats, $c_p/c_v = \gamma$, of nitrogen and oxygen described in the following paper was undertaken by a method substantially the same as that used previously with air and carbon dioxide, and described in an earlier communication.*

This consists in measuring the fall in temperature which occurs when a large volume of the gas is allowed to expand adiabatically. If a vessel filled with the gas at a pressure p_1, slightly greater than atmospheric, is put into communication with the free air, at a pressure p_2, by suitable means, so that the equalisation of pressures occurs as nearly as possible adiabatically, and if T_1 and T_2 are the absolute temperatures of the gas before and after expansion, then, *for an ideal gas*, it is known that

$$\gamma = c_p/c_v = \frac{\log p_1 - \log p_2}{(\log p_1 - \log p_2) - (\log T_1 - \log T_2)} \qquad (1)$$

Before considering the details of the method used in the present research reference may be made to the experiments of Mercer, in 1914, and of Shields, in 1917, supplementing the work discussed in the previous communication.

Mercer† used an expansion vessel of only 300 c.c. capacity and attempted to correct for the considerable errors introduced, owing to convection currents from the walls, by making a second determination with a vessel of twice the linear dimensions of the first, assuming that the error introduced was a linear function of this dimension. Twice the difference between the two results was therefore added to the first result. This correction for the errors introduced by the use of so small a vessel would seem inadequate. Mercer also omitted to correct for the divergence of the gases employed from the ideal state, on account of the "great variety of expressions" which might be used for the correction, and assumed that the latter would in any case be small. The validity of this assumption naturally depends on the degree of accuracy aimed at in the investigation, and in view of the circumstance that Mercer applied corrections for the tarnished condition of the bolometer wire, and other conditions, which raised his experimental value for air from 1·382 to 1·400, it is clear that a correction for the deviation of the gas from the ideal state, amounting to about 0·001, would not affect his result seriously. It may be noted that Mercer assumed an additive relation for γ in correcting his results with nitrous oxide for the air contained in it, and also assumed that the radiation corrections for gases would be in the inverse ratio of the thermal conductivities. In the first case the additive relation really applies to c_v, not γ, and the radiation corrections in different gases are in the ratio of the squares of the refractive indices, *i.e.*, practically unity.

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* J. R. Partington: 'Physikalische Zeitschrift,' vol. 14, p. 969 (1913); 'Roy. Soc. Proc.,' A, vol. 100, p. 27 (1921).

† H. N. Mercer: 'Proc. Phys. Society,' vol. 26, p. 155 (1914).

Shields* used a one litre vessel, and attempted to correct for the errors due to convection and radiation by assuming them to be a function of ΔT and therefore of Δp. Using different values of Δp, she extrapolated the apparent values of γ to zero pressure difference, assuming the relation to be "practically linear." This method of extrapolation has been criticised in the former communication, and appears to be uncertain. Some little uncertainty was also introduced by the use of a galvanometer with an appreciable period, and by the fact that the expansion is stated to be "oscillatory," in consequence of which the temperature is measured some definite time after the expansion is complete, which seems undesirable with such a small vessel. Shields used excess pressures of from 7 to 35 mm. of mercury, hardly sufficient to give really accurate results. The results obtained by using different thermo-junctions also differed somewhat widely, especially in the series of determinations for hydrogen at ordinary temperatures, in which case the values of γ varied from 1·3781 to 1·4014. When extrapolated to zero fall of temperature, however, the results were in good agreement, which indicates the magnitude of the correction introduced by extrapolation. The final values obtained were 1·4029 for air and 1·4012 for hydrogen at ordinary temperatures. The latter result in particular seems to be low, if compared with Lummer and Pringsheim's value of 1·4084, which is the only one to which much confidence may be attached.*

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* M. C. Shields: 'Physical Review,' vol. 10, p. 525 (1917).

In the present research, the expansion vessel, A, fig. 1, consisted of a spherical copper globe of about 60 litres capacity, provided with two lateral outlets.

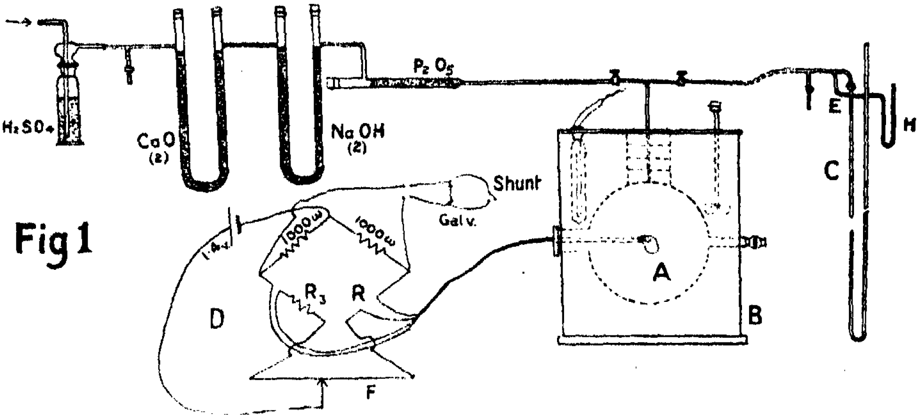

Fig 1

One, about 14 cm. long and 6 cm. diameter, was fitted with a heavy brass screw cap with fibre washer, which could be tightened by means of a pin spanner in order to make it gas-tight. The glass support of the bolometer wires fitted through a hole bored through the centre of this cap and the joint was made gas-tight by means of Faraday's cement.

The second outlet was of the same length, but 2·5 cm. diameter. This outlet was that through which the expansion occurred and was, in the earlier experiments, closed by a rubber stopper which could be pulled out by means of a cord. The gas was admitted to the globe by means of a narrow copper tube at the top.

The globe was immersed in a water-bath, B, of galvanised iron. The method of supporting the globe in the water-bath was essentially the same as that previously described. Electrical heating by means of a 250 watt radiator lamp immersed in the bath was used, and the temperature controlled by a modified Lowry toluene thermo-regulator with electrical contacts operating a relay. By means of this apparatus the temperature of the bath was kept constant to less than 0·01° C., the limit of accuracy of the thermometer employed.

The gases used were contained, initially at a pressure of 120 atmospheres, in cylinders fitted with reducing valves. The particular gas in use was purified in an appropriate manner, and dried by being passed through a wash-bottle of concentrated sulphuric acid and through large U-tubes containing, respectively, quicklime, solid caustic soda, and phosphorus pentoxide. The latter was not specially purified.

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* Some experiments by the authors, not yet completed, point to a value of γ for hydrogen at least as high as that found by Lummer and Pringsheim.

The principal manometer, C, by means of which the excess of the pressure of gas in the globe over the atmospheric pressure was measured, was a long glass U-tube fixed to a board and filled with colourless paraffin oil of high boiling point, the density of which at t ° C. was found to be $0 \cdot 8547 - 0 \cdot 0005128\, t$, determined by careful measurements of the density at 17° C. and at 24·8° C., the latter in a thermostat. The weight of oil contained in the bottle was compared with the weight of distilled water it contained at the same temperature. The constants for water were assumed and the expansion of the bottle thus eliminated. The value for the density obtained was confirmed to 0·0001 by an independent determination of the density by the same method by Mr. F. W. Bury, and to 0·0007 by means of a (less accurate) Mohr's balance.

The levels of oil in the manometer were read to 0·01 cm. by means of a cathetometer with an accurately engraved brass scale. In order that the manometer might not be affected by heat from the water-bath, it was situated in a small room adjoining that in which the remainder of the apparatus was set up. The curtained windows of this room were always kept open whilst an experiment was in progress, and the manometer was screened from the direct rays of the sun. The temperature of the oil was determined by means of two calibrated thermometers attached to the top and bottom of the board supporting the manometer, respectively. In general they agreed to within 0·2° C. The mean of the readings of the two thermometers was taken as the temperature of the oil.

The atmospheric pressure, which is taken as the pressure p_2 after expansion, was determined to 0·01 cm. of mercury on a Fortin type barometer, in a room at the same altitude as the laboratory in which the experiments were conducted. The reading was corrected to 0° C., the excess pressure as determined by the manometer being also reduced to millimetres of mercury at that temperature. The initial pressure, p_1, was thus found by adding together this mercury value of the oil column and the corrected reading of the barometer.

The bolometer used to determine the fall in temperature on the expansion of the gas consisted of about 10 cm. of Wollaston wire of 0·01 mm. diameter. The effect of the leads was entirely eliminated by having a second piece, about 4 cm. long, attached to compensating leads, in the arrangement previously described.

The arrangement for supporting the bolometer wires was precisely similar to that previously used except that the part E was omitted (fig. 2 in previous paper). The wires were annealed by passing an electric current of about 2 amperes through them when soldered in position on the support.

The wire used was supplied by Messrs. Johnson, Matthey and Co., Ltd. Wires of 0·001 and 0·002 mm. supplied by this firm, and also by Hartmann and Braun, of Frankfort a/M, were tried, but without success, although such wires from the second source were used in the previous research. Wires of 0·01 mm. diameter were, therefore, employed in all the experiments. It was found necessary, as will be described later, to apply a correction to the recorded fall of temperature, on account of the appreciable lag shown by these wires.

The auxiliary mercury thermometer was the same as that previously used. It was carefully calibrated in a vertical position with the normal thermometer No. 58,241 (1914) of the German Reichsanstalt.* No emergent stem correction was necessary, as both thermometers were completely immersed in a thermostat, and in the actual experiments the thermometer was completely immersed in the water of the bath, suspended on a wire. Readings were made through a plate-glass window in the side of the tank.

The four copper leads of the bolometer were carried through a piece of rubber tubing to the resistance apparatus, D, consisting of a Post Office box by Gambrell Bros., London, with an accuracy of 1 in 1,000. The sensitiveness of the bridge was increased by the addition of a supplementary bridge, F, consisting of a piece of eureka wire soldered to copper terminals and fitted with a sliding contact, the whole insulated on blocks of paraffin wax. The slider was connected to the Leclanché cell which provided the current for the bridge, and the two end terminals to the resistance arm of the bridge, and one of the main leads of the bolometer, respectively. The bridge connections were otherwise as usual, the compensating leads being inserted in the resistance arm. The current passing through the bridge was approximately 2 milliamperes, which was insufficient to cause any appreciable heating of the bolometer wire. The difference between the resistances of the two loops of the latter was about 120 ohms.

The galvanometer was an Einthoven "Saitengalvanometer" made by Edelmann of Munich, with a gold string 0·005 mm. diameter, resistance 130 ohms. The sensibility was 10^{-8} ampere per scale division, and one-tenth of a scale division could be estimated with the objective and eyepiece used. The field magnets were actuated by a constant current of two amperes taken from the 240-volt power mains, using a suitable resistance and ammeter in series. Connection with the bridge was made by means of a reversing key, and a shunt was provided for use in the preliminary adjustments. All the keys were insulated on blocks of ebonite and the galvanometer earthed to prevent interference from stray currents from the magnet system.

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* For the loan of this thermometer we are indebted to the Council of the Chemical Society.

In a determination the initial temperature of the bath was raised to about 22° C. and maintained at this temperature by the electric thermostat arrangement. The gas under experiment was forced into the globe to an excess pressure of about 6 cms. of mercury. A preliminary rough adjustment of pressure was made by means of the small mercury manometer (H, fig. 1) and the pressure finally adjusted to its required value. This procedure was adopted in order to avoid continual large disturbances of the oil in the manometer, as it was somewhat viscous and considerable time was necessary for the level to become constant if large changes of level took place. The tube immediately above the levels was always moistened with oil before taking a reading, by a slight displacement of the levels of oil in the manometer.

When the resistance of the bolometer and the reading of the manometer had both become perfectly steady, showing that the temperature of the gas in the globe had become uniform, the manometer tap, E, was closed and the resistance on the bridge altered to such a value as was judged would correspond with that of the bolometer, immediately after the expansion had occurred. The galvanometer and battery keys of the Post Office box were depressed, the galvanometer being, of course, deflected in consequence. The gas was then allowed to expand, in the earlier experiments by pulling out the rubber stopper by means of a cord, and in the later experiments, as will be described, by opening a large stopcock. The galvanometer deflection then fell practically instantaneously to a position near the zero of the scale. This position was noted and the whole operation repeated, using the same excess pressure and initial temperature, but with a slight alteration of the sliding contact of the supplementary bridge, as indicated by the deflection obtained in the previous expansion. This was found more convenient than the method previously adopted, of altering the pressure.

When, after two or three trials, the deflection returned precisely to zero after expansion, the temperature of the bath, the levels of the manometer, the temperature of the latter, and the height of the barometer were carefully read. Sufficient water was then baled out of the bath to permit of the addition of ice, which was added until the galvanometer, with the bridge unaltered, was again steadily at zero, with all the ice melted. The water was kept in motion by means of the stirrer and the final adjustment of temperature was accomplished by adding a little more ice or by turning on the heating lamp for a few seconds. On account of the large mass of water in the bath this final temperature adjustment could be performed with accuracy. The temperature of the bath was then carefully read on the mercury thermometer and the measurement was completed.

A few determinations were first made with air in order to check the values obtained with the apparatus against those obtained in the former research. After a few preliminary experiments, the values obtained for γ' for air were 1·3928 and 1·3968, there being some uncertainty to within 0·05° in the measurement of the final temperature in the second determination.

These results being somewhat low, a correction was applied for the fact that the wires used in the bolometer might have an appreciable effect on the result on account of their larger heat capacity. Some experiments referred to in the earlier communication showed that the deflections obtained corresponding with the same fall of temperature with wires of different diameters were approximately in linear relation to the diameters.* In the case of wires of 0·001 and 0·01 mm. diameter respectively, the deflections were in the ratio 377/372, although the lag in the case of 0·01 mm. wires was insufficient to cause any visible sluggishness in the deflection of the galvanometer.

Whilst it seems desirable to make further experiments relative to the effect of the thickness of the wire used for the bolometer, this has so far been impossible owing to failure to obtain a good specimen of the thin wire, but experiments are still proceeding. Meanwhile, although the authors feel confident that the data quoted above are sensibly correct, it is necessary to regard the results involving this correction as being of a somewhat provisional nature, possibly requiring slight modification at some future date.

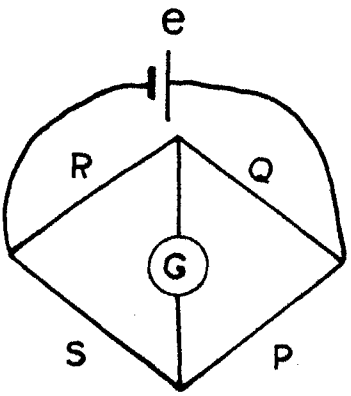

Fig. 2.

In fig. 2, representing the bridge, let R and S be the resistances of the ratio arms, P the resistance of the bolometer wire, and Q the balancing resistance in the box. Let the potential difference across the bridge be e and the resistance of the galvanometer, G. Then it has been shown by Adcock and Wells* that for the case where compensating leads are inserted in Q, where $R = S$, and where a "parallel" arrangement of the thermometer and compensating circuits is adopted:

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* 'Roy. Soc. Proc.,' A, vol. 100, p. 31 (1921).

$$V = e\,\frac{P - Q}{\left(1 + \frac{R}{G}\right)(P + Q) + R + \left(\frac{2}{G} + \frac{1}{R}\right)PQ} \tag{2}$$

where V is the potential difference across the galvanometer.

Then if C is the current flowing through the galvanometer:—

$$C = e\,\frac{P - Q}{P\left(G + R + 2Q + \frac{QG}{R}\right) + QG + RG + QR}. \tag{3}$$

In this expression, C and P, in the case under consideration, are the only variables.

Thus:

$$\frac{\Delta P_1}{\Delta P_2} = \frac{C_1}{C_2} \times \frac{K - C_2}{K - C_1}, \tag{4}$$

where

$$K = e\Big/\left(G + R + 2Q + \frac{QR}{G}\right).$$

In the case under consideration $C_2/C_1 = 372/377$, and C_1 and C_2 are of the order of $10^{-8} \times 15 = 1 \cdot 5 \times 10^{-7}$ amp. K is of the order of

$$1 \cdot 4/(100 + 1000 + 250 + 1000) = 6 \times 10^{-4} \text{ amp.}$$

The factor $(K - C_2)/(K - C_1)$ is therefore very nearly unity and we have:

$$\frac{\Delta P_1}{\Delta P_2} = \frac{C_1}{C_2}, \tag{5}$$

that is, if, after balancing the bridge, a variation occurs in the resistance of the bolometer wire, the current then flowing through the galvanometer will be proportional to the change of resistance of the wire, and therefore to the change in temperature. For small deflections, the deflection is proportional to the current flowing through the galvanometer,† and therefore the true final temperature of the gas will be given by the relation,

$$T_2 = T_1 - (T_1 - T_2')\,\tfrac{377}{372} \tag{6}$$

where T_1 is the initial temperature, T_2 the final temperature, and T_2' the apparent final temperature.

The two foregoing determinations were now recalculated, using the above correction. The calculation of all the following determinations was made in the way described in the previous paper (p. 42).

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* 'Philosophical Magazine,' vol. 45, p. 541 (1923).

† Crehore: 'Philosophical Magazine,' vol. 28, p. 210 (1914).

The two preliminary experiments with air gave $\gamma' = 1\cdot4004$ and $\gamma' = 1\cdot4038$. These results were considered in sufficiently close agreement with those previously obtained for air to form a test of the apparatus, and it was decided to proceed with the determination of the ratio of the specific heats of nitrogen.

Experiments with Nitrogen.

The nitrogen was supplied in cylinders by the British Oxygen Company. They stated its composition to be: nitrogen, 99·6 per cent.; oxygen, 0·2 per cent.; neon, 0·045 per cent.; helium, 0·15 per cent., by volume.

The oxygen was removed by passing the gas, after being taken from the cylinder by means of a reducing valve, through a heated hard glass tube containing copper turnings. A correction for the neon and helium present was applied to the final result. The gas was then dried, as already described, by tubes containing quicklime, caustic soda, and phosphorus pentoxide.

The following results were obtained for nitrogen:—

Results with Nitrogen. Series I.

p_1.	p_2.	T_1.	T_2.	γ' (uncorrected).
mm.	mm.	°	°	
805·6	744·7	295·10	288·52	1·4020
801·3	740·3	295·04	288·44	1·3997
803·5	741·6	295·16	288·49	1·3990*
829·5	768·4	295·22	288·79	1·4045*
832·84	772·17	295·30	288·97	1·4015
831·63	771·52	295·30	289·03	1·4007
826·33	765·54	295·19	288·78	1·4030
817·12	756·72	295·23	288·82	1·3999
812·65	752·43	295·25	288·84	1·3987*
810·60	752·20	295·24	288·76	1·4028

Mean $\gamma' = 1\cdot4012 \pm 0\cdot0006$†

* Rejected later. † Including results marked *.

After the completion of the results for oxygen, a second series was obtained for nitrogen, in order to obtain a result with a smaller mean error than the above, and in order to determine whether the results obtained for nitrogen were too high owing to "overshooting" of the expansion, as the first results obtained with oxygen were found to be.[*]

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[*] See later, p. 239.

The following results were obtained :—

Results with Nitrogen. Series II.

p_1.	p_2.	T_1.	T_2.	γ' (uncorrected).
mm.	mm.	°	°	
803·81	745·17	296·27	289·93	1·4000
815·86	757·22	296·26	289·99	1·4022
831·98	772·10	296·26	289·97	1·4025
830·96	772·00	296·26	290·08	1·4011
833·54	775·35	296·27	290·18	1·4025

From these results it was evident that " overshooting " had not previously taken place in the case of the nitrogen. The mean of both series was therefore taken.

Rejecting now the third, fourth and ninth results of the first series, as diverging too greatly from the mean value, we obtain from the two series a mean value of $\gamma' = 1\cdot4015 \pm 0\cdot0003$.

This result now requires correction for the effects of radiation and for the divergence of nitrogen from the ideal state.

In order to correct for radiation, we have to increase the value of γ' by 0·0021, as has been shown in the earlier communication. Applying this correction, therefore, we obtain :—

$$\gamma' \text{ for nitrogen at } 20^\circ \text{ C.} = 1\cdot4015 + 0\cdot0021 = 1\cdot4036 \pm 0\cdot0003.$$

The value of $\gamma = c_p/c_v$ was also shown to be given by the equation

$$\gamma = \gamma' [1 + (\gamma' - 1) \tfrac{27}{32} \pi\tau^3] = \gamma'\phi, \tag{7}$$

a relation deduced from the characteristic equation of D. Berthelot, where

$$\pi = (p_1 + p_2)/2p_c, \text{ and } \tau = 2T_c/(T_1 + T_2), \tag{8}$$

p_c and T_c being the critical constants. In the case of nitrogen, $p_c = 33\cdot0$ atm., $T_c = 126\cdot5^\circ$ abs. The value of ϕ at 1·03 atm. pressure and 20° C. is therefore 1·00086. From this we find :

$$\gamma = c_p/c_v \text{ for nitrogen at } 20^\circ = 1\cdot4048 \pm 0\cdot0003.$$

This result still requires correction for the small quantities of helium and neon in the nitrogen.

Whilst for a mixture of gases the ratio of the specific heats cannot be regarded as the mean of the values for the constituent gases, the specific heat at constant volume may be so regarded in correction terms. In order, therefore, to correct for the presence of the helium and neon we must first calculate the specific heat of the sample of nitrogen at constant volume.

The specific heats at constant volume and at constant pressure may be calculated from the ratio $c_p/c_v = \gamma$, when the difference, $c_p - c_v$, or, more conveniently, $M(c_p - c_v) = C_p - C_v$, where M is the molecular weight, is known. This may be obtained from Berthelot's equation :—

$$C_p - C_v = 1 \cdot 985 \left(1 + \tfrac{27}{16} \pi \tau^3\right) = 1 \cdot 985 \, \phi' \text{ gram cal.,} \tag{9}$$

where π and τ have the values given by (8).[*]

In the case of nitrogen at 20°, $\phi' = 1 \cdot 0043$, hence $C_p - C_v = 1 \cdot 9935$ (15°) grm. cals., whence $C_v = 1 \cdot 9960/0 \cdot 4048 = 4 \cdot 9247$, for the actual gas. Now the percentage composition by volume of a mixture of gases is also the percentage molecular composition. Moreover we may take the molecular specific heat at constant volume for both helium and neon to be 3·0 with sufficient accuracy, and the nitrogen contains 0·195 per cent. by volume of inert gas. Therefore the value of C_v for pure nitrogen will be

$$(4 \cdot 9247 - 3 \cdot 0 \times 0 \cdot 00195)/0 \cdot 99805 = 4 \cdot 9286.$$

Thus $C_p = 4 \cdot 9286 + 1 \cdot 9935 = 6 \cdot 9221$. From these figures for pure nitrogen at 20° C. and 1 atm. pressure :

$$\gamma = C_p/C_v = 1 \cdot 4045 \pm 0 \cdot 0003.$$

The values of the specific heats per 1 gram of nitrogen will be

$$c_p = 6 \cdot 9221/28 \cdot 02 = 0 \cdot 2470 \text{ grm. cal., and}$$
$$c_v = 4 \cdot 9286/28 \cdot 02 = 0 \cdot 1759 \text{ grm. cals.}$$

The work done by former investigators on the specific heats of nitrogen is as follows. Masson,[†] in 1858, calculated the ratio of the specific heats from the velocity of sound in the gas, obtained by sounding an organ pipe in an atmosphere of nitrogen. He obtained a value of 1·415 for γ, which is unreliable. Masson obtained identical results for all the permanent diatomic gases.

Regnault[‡] found a value of 0·2375 for the mean c_p for air between 15° and 200° C., and 0·2175 as the mean of two determinations for oxygen, between 15° and 200°. Taking air to be 80 per cent. nitrogen and 20 per cent. oxygen by volume, he obtained the value of 0·2438 for c_p for nitrogen by calculation. This calculation was, however, made on the assumption, which cannot now be held to be correct, that c_p can be regarded as an additive quantity for a mixture of gases. It is not therefore possible to compare Regnault's value with that calculated from the results of the present research.

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[*] The value of R taken is 1·985 gram cal. (15°) per 1°.

[†] M. A. Masson: 'Annales de Chimie et de Physique,' vol. 53, p. 265 (1858).

[‡] V. Regnault: 'Mém. Acad. Sci.,' vol. 26, pp. 110, 303 (1862).

Cazin,[*] in 1862, determined the ratio of the specific heats directly, using the method of Clement and Desormes, and a somewhat improved apparatus. He obtained a value of $\gamma = 1\cdot41 \pm 0\cdot02$. This result requires correcting for radiation and deviation from the gas laws, but the correction is not within the limits of error of the experiments.

Holborn and Austin,[†] in 1905, determined the mean c_p for nitrogen over various ranges of temperature, by a calorimetric method. From their results we may calculate the *true* c_p at 20°, and obtain a value of 0·2319 grm. cals.

In 1907, Holborn and Henning,[‡] by a calorimetric method, determined the specific heat at constant pressure of nitrogen for the ranges, 1400° – 110° C., and 800° – 110° C. By extrapolation from these values they obtained the following expression for the *mean* specific heat between 0° and t° C.

$$c_p = 0\cdot2350 + 0\cdot000019\,t.$$

Whence c_p (true) at $20° = 0\cdot2358$ grm. cal.

Pier, in 1909,[§] obtained a value for the mean molecular heat at constant volume of nitrogen by mixing it in known proportions with electrolytic gas in a bomb, and finding the maximum pressure produced on explosion. From a series of results he obtained the expression for nitrogen:

$$\text{mean } C_v = 4\cdot900 + 0\cdot00045\,t.$$

If the validity of the extrapolation is assumed, this gives, at 20°, C_v (true) = 4·918 grm. cal.

Scheel and Heuse,[||] in 1913, determined c_p for nitrogen by a constant flow calorimetric method. They obtained the following results at 20° : $c_p = 0\cdot2492$; whence $C_p = 6\cdot983$; $C_v = 4\cdot989$ and $\gamma = 1\cdot400$. The second and third values were obtained by calculation from C_p using Berthelot's equation, and the following values for the critical constants of nitrogen : $T_c = 124°$ abs. ; and $p_c = 27\cdot5$ ats. Recalculating using the more recent values $T_c = 126\cdot5°$ and $p_c = 33\cdot0$ ats., we obtain $C_v = 4\cdot990$ and $\gamma = 1\cdot399$. It may be noted that the value found for c_p differs by about 5 per cent. from Holborn and Henning's value.

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[*] A. Cazin : 'Annales de Chimie et de Physique,' vol. 66, p. 206 (1862).

[†] Holborn and Austin : 'Wiss. Abhand. der Phys.-Tech. Reichsanstalt,' vol. 4, p. 133 (1905).

[‡] Holborn and Henning : 'Annalen der Physik,' vol. 23, p. 809 (1907).

[§] Pier : 'Zeitschrift für Elektrochemie,' vol. 15, p. 536 (1909).

[||] K. Scheel and W. Heuse : 'Annalen der Physik,' vol. 40, p. 473 (1913) ; 'Zeitschrift für Elektrochemie,' vol. 19, p. 593 (1913).

Schweikert,[*] in 1915, determined the velocity of sound in nitrogen at 20° C., by a modification of Kundt's method. He calculated 337·7 metres per second at 0° C., from which he calculated $\gamma = 1 \cdot 4061$. This requires correction and gives $\gamma = 1 \cdot 402$.

Dixon, Campbell and Parker[†] have determined the velocities of sound in nitrogen at temperatures from 0° to 1000° C. by actual measurements in a long coiled tube contained in a furnace. Their values are corrected for the difference of the velocity in a tube and in the free gas, and the ratio of the specific heats calculated from the corrected velocity by means of Berthelot's equation. At 0° they found 337·5 metres per second to be the velocity of sound in the free gas, and at 100°, 394·1 metres per second. In the calculation of the values of the specific heats from this velocity we obtain at 0°, $C_p/C_v = 1 \cdot 406$ and $C_v = 4 \cdot 914$, whilst at 100°, $C_p/C_v = 1 \cdot 402$ and $C_v = 4 \cdot 948$. Interpolation from these values gives at 20° C. : $C_p/C_v = 1 \cdot 405$ and $C_v = 4 \cdot 921$ in excellent agreement with the result of the present research.

Schulze and Rathjen,[‡] by another modification of Kundt's method, and correcting by van der Waals's equation, obtained as a mean of twelve experiments a value of $1 \cdot 4144 \pm 0 \cdot 0002$ for C_p/C_v for nitrogen at room temperature and atmospheric pressure. They used a value for air of 1·4044 in order to calculate the value for nitrogen. If we use the value for air, 1·4034, obtained in the previous research, and Berthelot's equation, we obtain for nitrogen a value of 1·412, which seems to be too high.

These results may now be tabulated with the results of the present research for purposes of comparison. Calculated values are enclosed in brackets.

Results with Nitrogen.

Observer.	γ.	c_p.	C_v.	Temp.
				° C.
Masson	1·415	—	—	—
Cazin	1·41 ± 0·02	—	—	—
Holborn and Austin	—	0·2319	—	20
Holborn and Henning	—	0·2358	—	20
Pier	—	—	4·918	20
Scheel and Heuse	(1·399)	0·2492	(4·990)	20
Schweikert	(1·402)	—	—	0
Dixon, etc.	(1·405)	—	(4·921)	20
Schulze and Rathjen	1·4120	—	—	—
Present Research	1·4045	(0·2470)	(4·929)	20

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[*] G. Schweikert: 'Annalen der Physik,' vol. 48, p. 593 (1915).

[†] Dixon, Campbell and Parker: 'Roy. Soc. Proc.,' A, vol. 100, p. 1 (1921).

[‡] F. A. Schulze and H. Rathjen: 'Annalen der Physik,' vol. 49, p. 451 (1916).

Our results are seen to be in excellent agreement with those of Dixon, Campbell and Parker, which appear to be more accurate than any of the other previous measurements described. This we regard as an important confirmation of the accuracy of our method.

Experiments with Oxygen.

The oxygen used was "electrolytic oxygen," compressed in cylinders and supplied by the British Oxygen Company. It contained as impurity only about 0·2 per cent. of hydrogen, which was removed by passing the gas, on its way to the drying tubes, through a hard glass tube containing heated platinised asbestos. The gas was dried by being bubbled through concentrated sulphuric acid and passed through tubes containing quicklime, solid caustic soda, and phosphorus pentoxide, as already described in the case of the nitrogen.

A series of fifteen results were first obtained for oxygen. The agreement was not so good as was desired, the values for γ', uncorrected for radiation and divergence from the gas laws, varying from 1·3892 to 1·4014.[*] These irregularities were not observed in the case of nitrogen. In addition to the erratic values obtained, difficulty was experienced in making the trial expansions for each determination, the deflections obtained in successive expansions, after slightly varying the position of the bridge slider, not being quite consistent. In order to eliminate this effect, it was decided to try a brass stopcock through which to make the expansion.

The aperture of the stopcock was rectangular, and about equal in area to a circular tube of 1 centimetre diameter. The expansion now took from ½ to 1 second to complete. The irregularities were then found to be eliminated completely, but the galvanometer deflection was about half a small scale division less than before, this difference corresponding to about 0·10° less fall in temperature.

With a view to determining which deflection could be regarded as correct the following experiments were carried out. An expansion was made using the stopcock, and a perfectly steady deflection obtained. The bridge was balanced so that immediately after expansion the deflection was zero. Another expansion was then made under exactly the same conditions, except that the usual full opening and rubber bung were used instead of the stopcock. (Diameter of outlet tube = 2·5 cms.) The deflection now obtained was not perfectly steady, but the immediate value was approximately half a small scale division larger than that obtained with the stopcock, thus confirming the result previously obtained. A tube of 1·1 cm. diameter was now tried, with a rubber stopper. The deflection was perfectly steady, and of the same magnitude as that obtained using the stopcock. Finally, a tube of intermediate diameter (1·6 cm.) was used. The deflection was intermediate between those already obtained, but was not steady, and was not consistent for two successive expansions. It was therefore decided to use the stopcock for future work, as it was evident from the foregoing experiments that slight irregularities had been introduced owing to the gas "overshooting" in the expansion through too large an aperture. The occasional use of a still smaller aperture, caused by the stopcock not opening fully, did not modify the deflection obtained, although the expansion was in that case considerably slower.

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[*] It may be desirable to point out that the degree of reproducibility here attained is more satisfactory than that of previous experimenters, but it is not regarded as sufficient for the accuracy aimed at in the present research.

The numerical results obtained in the experiments with oxygen just described were as follows :—

Initial temperature in each case = 23·16° C.

Using stopcock.—Final temperature = 16·99°. $\gamma' = 1·3919$.

Using rubber stopper and full opening (2·5 cm.).—Final temperature = 16·88°. $\gamma' = 1·4019$.

As was previously mentioned, this overshooting was not observed in the case of nitrogen. It thus did not seem probable that the results so obtained would have to be discarded. Their validity was demonstrated by the second series of results when the stopcock was used, which gave a mean value for the ratio of the specific heats almost identical with that from the first series.

A series of results for oxygen was now obtained.

Results with Oxygen.

p_1.	p_2.	T_1.	T_2.	γ' (uncorrected).
mm.	mm.	°	°	
826·19	766·43	296·23	290·04	1·3912
819·34	759·58	296·25	290·00	1·3919
810·40	750·45	296·25	289·92	1·3909
809·22	749·88	296·31	290·04	1·3905
819·88	760·05	296·32	290·07	1·3916
818·59	758·63	296·29	290·03	1·3902
817·63	758·63	296·21	290·04	1·3920
823·15	763·31	296·21	290·00	1·3904
821·69	762·14	296·34	290·16	1·3921
820·17	762·05	296·33	290·28	1·3903

Mean $\gamma' = 1,3911 \pm 0·0002$

In order to check still further the previous decision that the higher results obtained with the rubber stopper and large aperture were in reality due to overshooting during expansion, a determination was now made with oxygen, using about half the former excess pressure. Under these conditions it might be expected that the overshooting would not be so likely to occur, and the same result would probably be found whether the stopcock or the rubber stopper was used. It was found that the deflection when the rubber stopper was used, though not quite so steady, was, within the possible accuracy of the measurement, identical with that using the stopcock. This determination gave the following figures : $p_1 = 787 \cdot 17$ mm. ; $p_2 = 756 \cdot 87$ mm. ; $T_1 = 296 \cdot 25°$; $T_2 = 293 \cdot 02°$; giving $\gamma' = 1 \cdot 3873$; a result of the same order as the results obtained at the higher pressure using the stopcock, and thus confirming the assumption regarding overshooting.

The above mean result requires correction for radiation and for divergence of oxygen from the ideal state, as in the case of the nitrogen. For oxygen, $p_c = 50 \cdot 2$ atm., $T_c = 154 \cdot 25°$ abs. Thus at 20° C. and 1·04 atm. pressure, $\phi = 1 \cdot 0010$. The radiation correction is 0·0021, and therefore

$$\begin{aligned} \gamma &= c_p/c_v \text{ for oxygen at } 20° \text{ and 1 atm. pressure.} \\ &= (1 \cdot 3911 + 0 \cdot 0021)\, 1 \cdot 0010 \pm 0 \cdot 0001. \\ &= 1 \cdot 3946 \pm 0 \cdot 0002. \end{aligned}$$

Calculating the specific heats at constant volume and at constant pressure, as in the case of the nitrogen, we have :—

$$\phi' = 1 \cdot 0051, \text{ hence } C_p - C_v = 1 \cdot 9951 \text{ grm. cals.}$$

Thus $$C_v = 1 \cdot 9951/0 \cdot 3946 = 5 \cdot 0559 \text{ grm. cals.}$$

$$C_p = 5 \cdot 0559 + 1 \cdot 9951 = 7 \cdot 0510 \text{ grm. cals.}$$

For 1 gram of oxygen these become

$$c_v = 0 \cdot 1581 \text{ grm. cals.} \quad \text{and} \quad c_p = 0 \cdot 2294 \text{ grm. cals.}$$

These results may now be compared with those obtained by other workers.

Masson obtained the same value, 1·415, for γ for oxygen and for nitrogen. Dulong,[*] in 1829, also determined the ratio of the specific heats for oxygen by a method similar to that of Masson, and obtained as a mean result, $\gamma = 1 \cdot 415$. Regnault, as already indicated, obtained calorimetrically for c_p the value 0·2175 for oxygen, the mean of two determinations. If we increase this by 1/160 of its value, as considered necessary by Leduc[†] in the case of air, on account of Regnault's neglect to take account of the expansion of the gas in passing from the heater to the calorimeter, we obtain 0·2188 cals. Cazin obtained 1·41 ± 0·02 for γ for oxygen.

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[*] Dulong : 'Annales de Chimie et de Physique,' vol. 41, p. 113 (1829).

[†] Leduc : 'Comptes Rendus,' vol. 126, p. 1860 (1898).

An accurate direct determination of c_p/c_v for oxygen was made by Lummer and Pringsheim* in 1894. They obtained the value, $\gamma = 1\cdot3977$, corrected for radiation and deviations from the gas laws. They used, however, commercial oxygen ("käuflicher Sauerstoff"), containing probably about 9 per cent. of nitrogen by volume. Lummer and Pringsheim's results have been recalculated using the method of correction by Berthelot's equation employed in the present research. The results were practically identical with those using $t^\circ\,\mathrm{C} + 1/\alpha$, where α is the coefficient of expansion of the gas, instead of the absolute temperature, the method adopted by Lummer and Pringsheim. If we correct their value for the presence of the nitrogen, using the method employed in the present paper in the case of the determinations for nitrogen, we obtain 1·3970, using the value of C_v for nitrogen calculated from the results obtained in the present research. Correction for small quantities of the inert gases present in the "commercial oxygen" would, of course, further reduce this result.

Holborn and Austin, in 1905, obtained a series of results for c_p (mean) for oxygen, by the method employed for nitrogen, from which we calculate c_p (true) at 20° to be 0·2195 grm. cals. Scheel and Heuse, in 1913, determined c_p for oxygen, by the calorimetric method, and obtained the following results at 20°: $c_p = 0\cdot2182$ grm. cals.; whence $C_p = 6\cdot982$ grm. cals.; $C_v = 4\cdot989$ grm. cals., and $\gamma = 1\cdot399$.

Schweikert, in 1915, by modification of Kundt's method, obtained 315·7 m.p.s. as the velocity of sound in oxygen at 0°, from which he calculates $\gamma = 1\cdot4049$. Correction gives 1·402 by Berthelot's equation by multiplying by ϕ''.

Tabulating the results in order to compare the results of the present research with those obtained by other workers we have:—

Results with Oxygen.

Observer.	γ.	c_p.	C_v.	Temp.
				° C.
Masson	1·415	—	—	
Dulong	1·415	—		—
Regnault	—	0·2188	—	15–200
Cazin	1·41 ± 0·02	—	—	
Lummer and Pringsheim	1·3970 ± 0·0004	—		—
Scheel & Heuse	(1·399)	0·2182	(4·989)	20
Holborn and Austin	—	0·2195	—	20
Schweikert	1·402	—	—	0
Present research	1·3946 ± 0·0002	(0·2204)	(5·056)	20

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* O. Lummer and E. Pringsheim: 'Annalen der Physik,' vol. 64, p. 555 (1898).

A portion of the absorption of heat represented by c_p in the case of an imperfect gas is used in performing intermolecular work due to attractions existing between the gas molecules. The correction to the ideal state can be made from the following formula, derived from Berthelot's equation :—

$$C_v^0 \text{ (ideal)} = C_v - \tfrac{27}{32} R \pi \tau^3 \qquad (10)$$

$$C_p^0 \text{ (ideal)} = C_v^0 + 1 \cdot 985 \text{ grm. cals.} \qquad (11)$$

$$\gamma_0 \text{ (ideal)} = C_p^0 / C_v^0 . \qquad (12)$$

The values of $(27/32) \times R \pi \tau^3$ at 20° are : for nitrogen, 0·0042 ; for oxygen, 0·0050. Thence :—

	c_v.	c_p.	C_v.	C_p.	C_v^0.	C_p^0.	γ.	γ_0.
Nitrogen at 20° C.	0·1759	0·2470	4·929	6·922	4·925	6·910	1·4045	1·4030
Oxygen at 20° C.	0·1581	0·2204	5·056	7·051	5·051	7·036	1·3946	1·3930

A check on the above figures is the calculation of the values for air from the determined values for nitrogen and oxygen tabulated above.

Assuming that C_v for air is composed additively of the values of C_v for the constituent gases, and that air has the following composition by volume :— $N_2 = 78 \cdot 1$ per cent., $O_2 = 21 \cdot 0$ per cent., $A = 0 \cdot 9$ per cent., and that C_v for argon is 3·0, we find :—

$$\begin{aligned} C_v \text{ (calculated for air)} &= 4 \cdot 929 \times 0 \cdot 781 + 3 \cdot 0 \times 0 \cdot 009 + 5 \cdot 056 \times 0 \cdot 21 \\ &= 4 \cdot 939 \text{ grm. cals.} \end{aligned}$$

Leduc* uses substantially this method in order to calculate the value of the ratio of the specific heats for a mixture of gases from the known values for the constituent gases.

As C_v is not absolutely independent of pressure, the value of C_v for oxygen at 1/5 atmosphere pressure, and that for nitrogen at 4/5 atmosphere should be used in the above calculation. These values may be calculated from the relation,

$$C_{v_2} - C_{v_1} = R \tfrac{27}{32} \tau^3 (\pi_2 - \pi_1) \qquad (13)$$

derived from Berthelot's equation. The correction is, however, so small as to be within the limits of experimental error.

Before comparing the result calculated above with that obtained for air directly, it is necessary to refer to an arithmetical error in the previous com-

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* Leduc : 'Comptes Rendus,' vol. 160, p. 338.

munication.* **The paragraph on p. 46, dealing with the calculation of the specific heats at constant volume and constant pressure, should read as follows :—**

"In the case of air at 17°, $\phi' = 1 \cdot 0042$, hence $C_p - C_v = 1 \cdot 993$ grm. cal. The values for 1 grm. of air are : $c_p - c_v = 1 \cdot 993/28 \cdot 99 = 0 \cdot 06875$ grm. cal., $c_v = 0 \cdot 06875/0 \cdot 4034 = 0 \cdot 1704$ grm. cal., $c_p = 0 \cdot 1704 + 0 \cdot 0687 = 0 \cdot 2391$ grm. cal."

The molecular heats corresponding to these values are therefore $C_v = 4 \cdot 947$ and $C_p = 6 \cdot 933$ grm. cals.

It will thus be seen that the values of C_v for air from the value of γ observed directly, and that calculated from the values of γ determined for nitrogen and oxygen, are in excellent agreement.

It is also necessary to refer to a second arithmetical error in the previous paper. In calculating the "ideal" values for air and carbon dioxide the values of $(27/32) \times R\pi\tau^3$ at 17° are : for air, 0·0042 ; for carbon dioxide, 0·0264. We can thus correct the table on p. 49 as follows :—

	c_v.	c_p.	C_v.	C_p.	C_v^0.	C_p^0.	γ.	γ_0.
Air at 17° C.	0·1704	0·2391	4·940	6·933	4·936	6·921	1·4034	1·4021
Carbon dioxide at 17° C.	0·1531	0·1996	6·744	8·782	6·718	8·703	1·3022	1·2955

Finally the authors desire to thank the Government Grant Committee of the Royal Society for a grant which has largely defrayed the expenses of the investigation.

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* 'Proc. Roy. Soc.,' A, vol. 100 (1921).

The Lattice Points of a Circle.

By G. H. Hardy, F.R.S., Savilian Professor of Geometry in the University of Oxford, and E. Landau, Professor of Mathematics in the University of Göttingen.

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1. *Introduction.*

1.1. We denote by $r(n)$ the number of representations of n as the sum of two squares, representations which differ only in sign or order being counted as distinct;[*] or, what is the same thing, the number of integral solutions of

$$u^2 + v^2 = n, \tag{1.11}$$

or the coefficient of z^n in the expansion

$$(\vartheta(z))^2 = (1 + 2z + 2z^4 + 2z^9 + \dots)^2 = \sum_0^\infty r(n) z^n. \tag{1.12}$$

If x is not an integer, or is negative, we write $r(x) = 0$.

By $\mathrm{A}(x)$ we denote the number of lattice-points, or points with integral co-ordinates, inside or on the circumference of the circle

$$u^2 + v^2 = x \quad (x > 0); \tag{1.13}$$

so that

$$\mathrm{A}(x) = \sum_{\nu=0}^{[x]} r(\nu) = \sum_{0 \leqq \nu \leqq x} r(\nu). \tag{1.14}$$

We write also $\overline{\mathrm{A}}(x) = \mathrm{A}(x)$ if x is not integral, and

$$\begin{aligned}\overline{\mathrm{A}}(x) &= r(0) + \dots + r(x-1) + \tfrac{1}{2}r(x) \\ &= \sum_{0 \leqq \nu \leqq x}{}' r(\nu) = \mathrm{A}(x) - \tfrac{1}{2}r(x) = \tfrac{1}{2}\{\mathrm{A}(x-0) + \mathrm{A}(x+0)\}\end{aligned} \tag{1.15}$$

if x is integral; and

$$\mathrm{P}(x) = \mathrm{A}(x) - \pi x, \qquad \overline{\mathrm{P}}(x) = \overline{\mathrm{A}}(x) - \pi x. \tag{1.16}$$

It is known, after Gauss[†] that $\mathrm{P}(x) = O(x^{\frac{1}{2}})$, after Sierpiński[‡] that $\mathrm{P}(x) = O(x^{\frac{1}{3}})$, after van der Corput[§] that $\mathrm{P}(x) = O(x^{\Theta})$, where Θ is some number less than $\frac{1}{3}$, and after Hardy* and Landau† that $P(x) \neq O(x^{\alpha})$, where α is any number less than $\frac{1}{4}$.

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[*] $0 = 0^2 + 0^2$, $1 = (\pm 1)^2 + 0^2 = 0^2 + (\pm 1)^2$, and $5 = (\pm 2)^2 + (\pm 1)^2 = (\pm 1)^2 + (\pm 2)^2$ so that $r(0) = 1$, $r(1) = 4$, $r(5) = 8$.

[†] C. F. Gauss, "De nexu inter multitudinem classium, in quas formae binariae secundi gradus distribuuntur, earumque determinantem," Werke, vol. 2, pp. 269–291 (277).

[‡] W. Sierpiński, "O pewnem zagadnieniu z rachunku funkcyj asymptotycznych," 'Prace matematyczno-fizyczne,' vol. 17, pp. 77–118 (1906).

[§] J. G. van der Corput, "Neue zahlentheoretische Abschätzungen," 'Math. Annalen,' vol. 89, pp. 215–254 (1923).

1.2. In this memoir we are not concerned with the problem of the order of magnitude of $P(x)$, but with an identity which expresses $\bar{P}(x)$ as an infinite series of Bessel functions, viz.—

$$\bar{P}(x) = \sqrt{x} \sum_{\nu=1}^{\infty} \frac{r(\nu)}{\sqrt{\nu}} J_1(2\pi\sqrt{\nu x}). \qquad (1.21)$$

This identity was first stated by Voronoï,‡ who expressly disclaimed possessing an accurate proof, and only two proofs have been published, each of which presents very serious difficulties of its own, particularly when x is an integer. The first, by Hardy,§ depends on the theory of analytic functions, Cauchy's theorem, and the general theory of Dirichlet's series of type $\Sigma a_n e^{-s\sqrt{n}}$; and in particular on a very difficult theorem of Marcel Riesz.|| The second, by Landau,¶ involves real analysis only, and is in principle simpler; but, like all proofs based upon the so-called 'Pfeiffer's method,' it involves complicated distinctions between different geometrical figures, and is intricate and difficult in detail.

Our primary object has been to reduce the proofs of (1.21), both complex and real, to something like their simplest forms, and the two proofs we now present are each much simpler than any known before. In particular they present no more difficulty for integral than for non-integral values of x. We have also been able, in simplifying the proofs, to add considerably to the precision of the result.

In §2 we give a proof based upon Cauchy's theorem, which makes no appeal to Riesz's or any similar theorem, and is as straightforward as it is reasonable to expect. The proof shows incidentally that the convergence of

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* G. H. Hardy, "On the expression of a number as the sum of two squares," 'Quarterly Journal of Math.,' vol. 46, pp. 263–283 (1915).

† E. Landau, "Über die Gitterpunkte in einem Kreise (II)," 'Göttinger Nachrichten,' pp. 161–171 (1915).

‡ G. Voronoï, "Sur le développement, à l'aide des fonctions cylindriques, des sommes doubles $\Sigma f(pm^2 + 2qmn + rn^2)$, où $pm^2 + 2qmn + rn^2$ est une forme positive à coefficients entiers," 'Verhandlungen des dritten Int. Math.-Kongresses in Heidelberg,' pp. 241–245 (1905).

§ G. H. Hardy, *l.c. supra* (f.n.*).

|| For full proofs of this theorem see H. Cramér, "Über das Teilerproblem von Piltz," 'Arkiv for Mat.,' vol. 16, no. 21, pp. 1–40 (1922); and A. Walfisz, "Über die summatorischen Funktionen einiger Dirichletscher Reihen," 'Dissertation,' Göttingen (1922).

¶ E. Landau, "Über die Gitterpunkte in einem Kreise (III)," 'Göttinger Nachrichten,' pp. 109–134 (1920).

the series is uniform in any interval free from integral values of x, and that the remainder after n terms is $O(n^{-\frac{1}{4}+\epsilon})$ for every positive value of ϵ. It shows also the genesis of the non-uniformity of convergence for integral values of x, and of the 'Gibbs phenomenon' associated with this non-uniformity; but we have not laid any particular stress on these points in this section, since we can obtain still more precise information by our second method.

The next section (§3) is devoted to a proof, by a new method which possesses some interest of its own, of the formula

$$P_1(x) = \int_0^x P(y)\,dy = \frac{x}{\pi} \sum_{\nu=1}^{\infty} \frac{r(\nu)}{\nu} J_2(2\pi\sqrt{\nu x}). \tag{1.22}$$

This identity is, owing to the absolute convergence of the series, very much easier to prove than (1.21); and it is required for the proof of (1.21) given in §4.*

Finally, in §4 we deduce (1.21) from (1.22) by real analysis. We begin by proving a new identity, viz.—

$$\begin{aligned}\overline{P}(x) = \sqrt{x} \sum_{1 \leqq \nu \leqq x_1} \frac{r(\nu)}{\sqrt{\nu}} J_1(2\pi\sqrt{\nu x}) \\ + J_0(2\pi\sqrt{xx_1}) - \sqrt{\frac{x}{x_1}}\, P(x_1)\, J_1(2\pi\sqrt{xx_1}) - \frac{\pi x}{x_1} P_1(x_1)\, J_2(2\pi\sqrt{xx_1}) \\ + x \sum_1^{\infty} \frac{r(\nu)}{\nu} \int_{2\pi\sqrt{xx_1}}^{\infty} J_3(t)\, J_2\left(t\sqrt{\frac{\nu}{x}}\right) dt. \quad (1.23)\end{aligned}$$

The last series is absolutely convergent, and we are thus able to deduce from (1.23) very precise information concerning the series (1.21). This information is embodied in Theorems 2 and 3. These theorems show—

(1) that the series is convergent for every value of x;

(2) that it is uniformly convergent throughout any interval free from integral values of x;

(3) that the remainder after n terms is $O(n^{-\frac{1}{4}})$ for every value of x;

and (4) that this last result holds uniformly in any interval free from integral values of x.

They also exhibit explicitly the non-uniformity of the convergence of the series near an integral value of x, and the nature and magnitude of its Gibbs phenomenon.

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* The simplest proof of (1.22) on other lines is that given by Landau, "Über die Gitterpunkte in einem Kreise," 'Math. Zeitschrift,' vol. 5, pp. 319-320 (1919).

2. *Proof of the identity by complex integration.*

2.1. In this section we assume

(1) the fundamental properties of the functions $J_0(z)$ and

$$H_1(z) = H_1^{(1)}(z) = J_1(z) + iY_1(z) \tag{2.11}$$

for complex values of z;

(2) the value of a definite integral calculated by Weber;

(3) a special case of the formulæ of linear transformation of the theta-functions.

Our notation, so far as Bessel functions are concerned, is that of Prof. Watson's standard treatise.*

2.2. LEMMA 1. *If* $s = \sigma + it$, $\sigma > 0$, *then*

$$f(s) = \sum_1^\infty r(\nu)\sqrt{\nu}\, H_1(2\pi is\sqrt{\nu}) = \frac{1}{\pi^2 s} - \frac{1}{\pi^3 s^3} - \frac{s}{\pi^3}\sum_1^\infty \frac{r(\nu)}{(s^2+\nu)^2}. \tag{2.21}$$

Since

$$H_1(2\pi is\sqrt{\nu}) = O(|s|^{-\frac{1}{2}}\nu^{-\frac{1}{4}}e^{-2\pi\sigma\sqrt{\nu}}),\dagger$$

for fixed σ and large ν, and uniformly in t, the first series is absolutely convergent. The second series is absolutely and uniformly convergent throughout any finite domain free from poles of individual terms, and affects the continuation of $f(s)$ all over the plane.

In proving the lemma, we may suppose s positive. We have‡

$$H_1(2i\xi) = -\frac{1}{\pi\xi}\int_0^\infty \exp\left(-u - \frac{\xi^2}{u}\right) du. \tag{2.22}$$

In (2.22) write $\xi = \pi s\sqrt{m^2+n^2}$, multiply by $\sqrt{m^2+n^2}$, and sum with respect to m and n, omitting the pair $m = 0$, $n = 0$, and indicating this omission by a dash; and we obtain

$$f(s) = \sum_{-\infty}^{\infty}{}' \sqrt{m^2+n^2}\, H_1(2\pi is\sqrt{m^2+n^2})$$
$$= -\frac{1}{\pi^2 s}\int_0^\infty e^{-u}\sum_{-\infty}^{\infty}{}' \exp\left\{-\frac{\pi^2 s^2(m^2+n^2)}{u}\right\} du. \tag{2.23}$$

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* G. N. Watson, "A treatise on the theory of Bessel functions," Camb. Univ. Press, (1922).

† Watson, p. 198.

‡ Watson, pp. 78, 183; compare formulæ (8), p. 78 and (15), p. 183, taking $\nu = 1$.

The integral just written contains positive elements only, and the integration of the series is justified by (1) its uniform convergence over any finite interval $0 < u_0 \leqq u \leqq U$ and (2) the convergence of the result. Now*

$$\sum_{-\infty}^{\infty} \exp\left(-\frac{\pi^2 s^2 m^2}{u}\right) = \frac{\sqrt{u}}{s\sqrt{\pi}} \sum_{-\infty}^{\infty} \exp\left(-\frac{m^2 u}{s^2}\right);$$

and so

$$\Sigma' \exp\left\{-\frac{\pi^2 s^2 (m^2+n^2)}{u}\right\} = -1 + \Sigma \exp\left(-\frac{\pi^2 s^2 m^2}{u}\right) \Sigma \exp\left(-\frac{\pi^2 s^2 n^2}{u}\right)$$

$$= -1 + \frac{u}{\pi s^2} \Sigma \exp\left\{-\frac{(m^2+n^2)u}{s^2}\right\}. \tag{2.24}$$

Substituting from (2.24) into (2.23), isolating the term for which $m = 0, n = 0$, and integrating term by term,† we obtain

$$f(s) = \frac{1}{\pi^2 s} - \frac{1}{\pi^3 s^3} - \frac{s}{\pi^3} \sum_{-\infty}^{\infty}{}' \frac{1}{(s^2+m^2+n^2)^2},$$

which is (2.21).

2.3. LEMMA 2. *If* $c > 0$, $\xi > 0$, $\nu > 0$, *then*

$$I(c, \xi, \nu) = \frac{1}{2\pi i} \lim_{T\to\infty} \int_{c-iT}^{c+iT} H_1(2\pi i s\sqrt{\nu})\, J_0(2\pi i s\sqrt{\xi})\, ds = -\frac{\eta_\nu}{2\pi^2\sqrt{\nu}}, \tag{2.31}$$

where $\eta_\nu = 1 \ (\nu < \xi), \quad \eta_\nu = \frac{1}{2} \ (\nu = \xi), \quad \eta_\nu = 0 \ (\nu > \xi).$

Write $2\pi i s\sqrt{\nu} = z, \quad a = \sqrt{\xi/\nu}.$

Then
$$I = -\frac{1}{4\pi^2\sqrt{\nu}} \lim_{T\to\infty} \int_C H_1(z)\, J_0(az)\, dz, \tag{2.32}$$

where C is the line $-T \leqq x \leqq T$, $y = 2\pi c\sqrt{\nu} = \gamma$, described negatively, in the plane of $z = x + iy = re^{i\theta}$, provided that this limit exists.

We apply Cauchy's theorem to the rectangle whose vertices are T, $T + i\gamma$, $-T + i\gamma$, $-T$, excluding the origin by the semicircle $r = \rho$, $0 \leqq \theta \leqq \pi$; and make $\rho \to 0$, $T \to \infty$. If we observe that‡

$$H_1(z) = J_1(z) + \frac{2i}{\pi} J_1(z) \log \tfrac{1}{2}z - \frac{2i}{\pi z} + i\Phi(z),$$

where $\Phi(z)$ is an odd integral function of z, we find at once that, when $z = -x'$ is real and negative,

$$H_1(z) = H_1(-x') = J_1(x') - iY_1(x');$$

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* For a proof of this classical formula see, for example, E. Landau, "Handbuch der Lehre von der Verteilung der Primzahlen," p. 277 (1909).

† This procedure may of course be justified as before.

‡ Watson, p. 62, formula (3). Note that $\mathbf{Y}_1 = \pi Y_1$.

so that the contribution of the two parts of the real axis is

$$2\int_{\rho}^{\mathrm{T}} \mathrm{J}_1(x)\,\mathrm{J}_0(ax)\,dx \to 2\int_{0}^{\infty} \mathrm{J}_1(x)\,\mathrm{J}_0(ax)\,dx.$$

The contribution of the vertical sides tends to zero, since

$$\mathrm{H}_1(\pm\mathrm{T}+iy) = O\left(\frac{1}{\sqrt{\mathrm{T}}}\right),\ \mathrm{J}_0(\pm a\mathrm{T}+aiy) = O\left(\frac{1}{\sqrt{\mathrm{T}}}\right)$$

uniformly for $0 \leqq y \leqq \gamma^*$; and the contribution of the semicircle is in the limit

$$-\pi i \times -\frac{2i}{\pi} = -2.$$

Hence finally we obtain

$$\lim_{\mathrm{T}\to\infty}\int_{\mathrm{C}} \mathrm{H}_1(z)\,\mathrm{J}_0(az)\,dz = 2-2\int_{0}^{\infty} \mathrm{J}_1(x)\,\mathrm{J}_0(ax)\,dx. \tag{2.33}$$

But[†]

$$\int_{0}^{\infty} \mathrm{J}_1(x)\,\mathrm{J}_0(ax)\,dx = 0,\ \tfrac{1}{2},\ 1 \tag{2.34}$$

according as $a > 1$, $a = 1$, or $0 < a < 1$. From (2.32), (2.33), and (2.34) we deduce (2.31).

2.4. Lemma 3. *If $c > 0$, $\xi > 0$, then*

$$\lim_{\mathrm{T}\to\infty}\frac{1}{2\pi i}\int_{c-i\mathrm{T}}^{c+i\mathrm{T}} f(s)\,\mathrm{J}_0(2\pi is\sqrt{\xi})\,ds = -\frac{\bar{\mathrm{A}}(\xi)-1}{2\pi^2}. \tag{2.41}$$

We replace $f(s)$ by the series which defines it; and it is clear, after Lemma 2, that we have merely to justify term-by-term integration over the infinite range. In what follows c, ξ are fixed, and O's are uniform in the variables t, ν.

We have[*]

$$\mathrm{H}_1(2\pi is\sqrt{\nu}) = -\frac{e^{-2\pi s\sqrt{\nu}}}{\pi s^{\frac{1}{2}}\nu^{\frac{1}{4}}} + O\left(\frac{e^{-2\pi c\sqrt{\nu}}}{|t|^{\frac{3}{2}}\nu^{\frac{3}{4}}}\right) = O\left(\frac{e^{-2\pi c\sqrt{\nu}}}{|t|^{\frac{1}{2}}\nu^{\frac{1}{4}}}\right), \tag{2.42}$$

$$\begin{aligned}\mathrm{J}_0(2\pi is\sqrt{\xi}) &= \frac{e^{-\frac{1}{4}\pi i}}{\pi s^{\frac{1}{2}}\xi^{\frac{1}{4}}}\cos\left(2\pi is\sqrt{\xi}-\tfrac{1}{4}\pi\right) + O\left(\frac{1}{|t|^{\frac{3}{2}}}\right)\\ &= \frac{1}{2\pi s^{\frac{1}{2}}\xi^{\frac{1}{4}}}\left(e^{2\pi s\sqrt{\xi}}-ie^{-2\pi s\sqrt{\xi}}\right) + O\left(\frac{1}{|t|^{\frac{3}{2}}}\right) = O\left(\frac{1}{\sqrt{t}}\right).\end{aligned} \tag{2.43}$$

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[*] Watson, pp. 198, 199.

[†] Watson, p. 406.

We may simplify the problem twice; first by neglecting the second term in the approximation for H_1 (since

$$\int^{\infty} \Sigma r(\nu)\sqrt{\nu}\,.\,\frac{e^{-2\pi c\sqrt{\nu}}}{t^{\frac{1}{4}}\nu^{\frac{1}{4}}}\,.\,\frac{1}{\sqrt{t}}\,.\,dt$$

is convergent), and then (for a similar reason) neglecting the second term in the approximation for J_0.

The problem is thus reduced to that of inverting the order of integration and summation in

$$\lim_{T\to\infty}\frac{1}{2\pi i}\int_{c-iT}^{c+iT}\frac{e^{\pm 2\pi s\sqrt{\xi}}}{2\pi^2\xi^{1/4}s}\,\Sigma\, r(\nu)\,\nu^{\frac{1}{4}}e^{-2\pi s\sqrt{\nu}}\,ds\,;$$

and this is justified by a classical theorem of Hadamard in the theory of Dirichlet's series.*

The convergence is uniform in any interval free from integral values of ξ, and the non-uniformity for an integral value k of ξ arises solely from the term $\nu = k$. It is the same as that of

$$\frac{r(\nu)}{2\pi^2}\lim_{T\to\infty}\frac{1}{2\pi i}\int_{c-iT}^{c+iT}\frac{e^{as}}{s}\,ds$$

for $a = 0$, and the magnitude of the 'Gibbs phenomenon' is

$$\frac{r(\nu)}{2\pi^2}\,.\,\frac{2}{\pi}\int_0^{\pi}\frac{\sin t}{t}\,dt.$$

2.5. We consider the integral

$$\frac{1}{2\pi i}\int_C f(s)\,J_0(2\pi i s\sqrt{\xi})\,ds, \tag{2.51}$$

where C is the rectangle $\frac{1}{2} - iT$, $\frac{1}{2} + iT$, $-\frac{1}{2} + iT$, $-\frac{1}{2} - iT$, described positively, and

$$T^2 = \mu + \tfrac{1}{2}, \tag{2.52}$$

μ being a positive integer. We denote the sides of C, taken in order, by C_1, C_2, C_3, C_4. By Lemma 1, $f(s)$ is odd, so that

$$\frac{1}{2\pi i}\int_{C_1} + \frac{1}{2\pi i}\int_{C_2} = \tfrac{1}{2}S. \tag{2.53}$$

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* J. Hadamard, "Sur les séries de Dirichlet," 'Rendiconti del Circolo Mat. di Palermo,' vol. 25, pp. 326–330 (1908). The problem is that of proving the formula

$$\lim\frac{1}{2\pi i}\int_{c-iT}^{c+iT} f(s)\,\frac{e^{ws}}{s}\,ds = \sum_{\lambda_n \leqq w}{}' a_n$$

for a function $f(s)$ defined by an absolutely convergent Dirichlet's series $\Sigma a_n e^{-\lambda_n s}$. We do not require Perron's extension of the theorem to non-absolutely convergent series.

S being the sum of the residues of the integrand at the poles $s=0,\ \pm i\sqrt{\nu}$, where $\nu = 1, 2, \ldots, \mu$.

A straightforward calculation* shows that

$$S = \frac{1}{\pi^2} - \frac{\xi}{\pi} - \frac{\sqrt{\xi}}{\pi^2} \sum_{\nu=1}^{\mu} \frac{r(\nu)}{\sqrt{\nu}} J_1(2\pi\sqrt{\nu\xi}); \tag{2.54}$$

and

$$\frac{1}{2\pi i}\int_{C_1} \to -\frac{\bar{A}(\xi) - 1}{2\pi^2}, \tag{2.55}$$

when $T \to \infty$, by Lemma 3. If we assume for the moment that

$$\frac{1}{2\pi i}\int_{C_2} \to 0, \tag{2.56}$$

then (2.53), (2.54), and (2.55) give (1.21). The proof of the identity is thus reduced to the proof of (2.56).

2.6. We substitute for $f(s)$ its expression given by (2.21). Since

$$J_0(2\pi i s\sqrt{\xi}) = O(T^{-\frac{1}{2}}) \tag{2.61}$$

on C_2, the contribution of the first two terms of (2.21) is $O(T^{-\frac{3}{2}})$, and is therefore trivial; and we have to prove that

$$\int_{-\frac{1}{2}+iT}^{\frac{1}{2}+iT} J_0(2\pi i s\sqrt{\xi})\, sF(s)\, ds \to 0, \tag{2.62}$$

where

$$F(s) = \sum_{1}^{\infty} \frac{r(\nu)}{(s^2+\nu)^2}. \tag{2.63}$$

We write
$$F(s) = \sum_{1}^{\mu-1} + \sum_{\nu=\mu} + \sum_{\mu+1}^{2\mu} + \sum_{2\mu+1}^{\infty} = F_1 + F_2 + F_3 + F_4. \tag{2.64}$$

2.7. We have, on C_2,

$$|s^2+\nu|^2 = (\sigma^2+\nu-T^2)^2 + 4\sigma^2T^2. \tag{2.71}$$

In F_1, $\nu = \mu - N$, where $1 \leqq N \leqq \mu - 1$, and

$$(\sigma^2+\nu-T^2)^2 = (\sigma^2 - N - \tfrac{1}{2})^2 > N^2, \quad 4\sigma^2T^2 \geqq \sigma^2\mu.$$

Hence the contribution of F_1 is

$$O\left(T \,.\, T^{-\frac{1}{2}} \int_{-\frac{1}{2}}^{\frac{1}{2}} \sum_{N=1}^{\mu-1} \frac{r(\mu-N)}{N^2+\sigma^2\mu}\, d\sigma\right) = O\left(\mu^{\frac{1}{4}+\epsilon} \sum_{N=1}^{\mu} \int_0^{\infty} \frac{d\sigma}{N^2+\sigma^2\mu}\right)$$
$$= O\left(\mu^{\frac{1}{4}+\epsilon} \,.\, \frac{1}{\sqrt{\mu}} \,.\, \sum_{N=1}^{\mu} \frac{1}{N}\right) = O(\mu^{-\frac{1}{4}+\epsilon}). \tag{2.72}$$

---

* In calculating the residues we have to observe that the poles (apart from that at the origin) are double, and that $J'_0(x) = -J_1(x)$.

When $\nu = \mu$,

$$(\sigma^2 + \nu - T^2)^2 = (\sigma^2 - \tfrac{1}{2})^2 \geqq \tfrac{1}{16}, \quad 4\sigma^2 T^2 \geqq \tfrac{1}{16}\sigma^2\mu.$$

Hence the contribution of F_2 is

$$O\left(T \,.\, T^{-\frac{1}{2}} \int_{-\frac{1}{2}}^{\frac{1}{2}} \frac{r(\mu)}{1 + \sigma^2\mu}\, d\sigma\right) = O\left(\mu^{\frac{1}{4}+\epsilon} \,.\, \frac{1}{\sqrt{\mu}}\right) = O(\mu^{-\frac{1}{4}+\epsilon}). \qquad (2.73)$$

In F_3, $\nu = \mu + N$, where $1 \leqq N \leqq \mu$, and

$$(\sigma^2 + \nu - T^2)^2 = (\sigma^2 + N - \tfrac{1}{2})^2 \geqq (N - \tfrac{1}{2})^2 \geqq \tfrac{1}{4}N^2, \quad 4\sigma^2 T^2 \geqq \tfrac{1}{4}\sigma^2\mu.$$

Hence the contribution of F_3 is

$$O\left(T \,.\, T^{-\frac{1}{2}} \int_{-\frac{1}{2}}^{\frac{1}{2}} \sum_{N=1}^{\mu} \frac{r(\mu + N)}{N^2 + \sigma^2\mu}\, d\sigma\right) = O(\mu^{-\frac{1}{4}+\epsilon}), \qquad (2.74)$$

as with F_1.

Finally, in F_4, $\nu = \mu + N$, where $N > \mu$, and

$$(\sigma^2 + \nu - T^2)^2 = (\sigma^2 + N - \tfrac{1}{2})^2 \geqq (N - \tfrac{1}{2})^2 > \tfrac{1}{4}N^2 > \tfrac{1}{16}\nu^2;$$

and the contribution of F_4 is

$$O\left(T \,.\, T^{-\frac{1}{2}} \int_{-\frac{1}{2}}^{\frac{1}{2}} \sum_{2\mu}^{\infty} \frac{r(\nu)}{\nu^2}\, d\sigma\right) = O(\mu^{\frac{1}{4}+\epsilon} \,.\, \mu^{-1}) = O(\mu^{-\frac{3}{4}+\epsilon}). \qquad (2.75)$$

2.8. From (2.72)—(2.75) and (2.64) we deduce (2.62): the value of the integral is in fact $O(\mu^{-\frac{1}{4}+\epsilon})$. This completes the proof of (1.21).

It is plain that the argument of 2.5—2.7 is valid uniformly throughout any interval $0 < \xi_0 \leqq \xi \leqq \xi_1$, so that the only non-uniformity of the convergence of the series (1.21) is that discussed in 2.4. The series is therefore uniformly convergent in any interval free from integral values of ξ.

3. *The formula for* $A_1(x)$.

3.1. The series (1.22) is uniformly convergent in any interval $0 < x_0 \leqq x \leqq x_1$, and its sum is continuous. In proving (1.22), then, we may suppose without loss of generality that x is non-integral.

We denote the circle (1.13) by $K(x)$ or simply by K. We divide up the plane (u, v) by the network $u = \frac{1}{2}a$, $v = \frac{1}{2}b$, where a and b are integers, so that every square of the network contains (on its boundary) just one lattice point. We denote by q a complete or partial square of the network falling inside K. If q is not complete, we denote the corresponding complete square by Q. If q is complete, Q is identical with q.

We write

$$f = f(u) = f(u, \delta) = \sum_{-\infty}^{\infty} e^{-(m-u)^2/\delta^2} = \sum_{-\infty}^{\infty} c_m.$$

If (u, v) lies in q, and (μ, ν) is the lattice point of Q, we write

$$f(u)\,f(v) = \sum_{m,n} c_m c_n = c_\mu c_\nu + \Sigma' c_m c_n = F_Q(u, v) + \overline{F}_Q(u, v), \qquad (3.11)$$

the dashed summation extending over all pairs (m, n) other than (μ, ν).

The function $f(u)$ satisfies the identity[*]

$$f(u) = \delta\sqrt{\pi} \sum_{-\infty}^{\infty} e^{-m^2\pi^2\delta^2} \cos 2m\pi u. \qquad (3.12)$$

3.2. LEMMA 4. *If $\psi(u, v)$ is any continuous function, then*

$$J = \frac{1}{\delta^2}\iint_K f(u)\,f(v)\,\psi(u, v)\,du\,dv \to \pi\,\Sigma\,\psi(\mu, \nu) \qquad (3.21)$$

when $\delta \to 0$, the summation applying to all lattice points of K.

We have, by (3.11),

$$J = \Sigma \frac{1}{\delta^2}\iint_q F_Q\,\psi\,du\,dv + \Sigma \frac{1}{\delta^2}\iint_q \overline{F}_Q\,\psi\,du\,dv = \Sigma J_q + \Sigma \overline{J}_q, \qquad (3.22)$$

say. We prove first that

$$\Sigma \overline{J}_q \to 0. \qquad (3.23)$$

If M is the maximum of $|\psi|$ in Q, we have

$$|\overline{J}_q| \leqq \frac{M}{\delta^2}\iint_Q \overline{F}_Q\,du\,dv = \overline{I}_Q, \qquad (3.24)$$

say: We suppose that (μ, ν) is the south-west corner of Q; the proof in other cases differs only trivially. We have then

$$\overline{I}_Q = \frac{M}{\delta^2}\Sigma' \int_\mu^{\mu+\frac{1}{2}}\int_\nu^{\nu+\frac{1}{2}} \exp\left\{-\frac{(m-u)^2 + (n-v)^2}{\delta^2}\right\} du\,dv = \frac{M}{\delta^2}\Sigma' j_{m,n},$$

say. Here $j_{m,n}$ is equal to

$$\iint e^{-(U^2+V^2)/\delta^2}\,dU\,dV$$

extended over the square of side $\frac{1}{2}$ whose south-west corner is $m-\mu,\ n-\nu$. If m, n, vary in the manner prescribed by Σ', these squares cover simply a region of the plane no point of which is at a distance less than $\frac{1}{2}$ from the origin. Hence

$$\overline{I}_Q \leqq \frac{M}{\delta^2}\iint_{U^2+V^2 \geqq \frac{1}{4}} e^{-(U^2+V^2)/\delta^2}\,dU\,dV = \frac{M}{\delta^2}\int_0^{2\pi} d\theta \int_{\frac{1}{2}}^{\infty} r e^{-r^2/\delta^2}\,dr$$

$$= \pi M e^{-1/4\delta^2} \to 0. \qquad (3.25)$$

---

[*] See for example Landau, *l.c.* (p. 248, f.n.*).

From (3.24) and (3.25) we deduce (3.23). On the other hand

$$\mathrm{J}_q = \frac{1}{\delta^2}\iint_q \psi \exp\left\{-\frac{(\mu-u)^2+(\nu-v)^2}{\delta^2}\right\} du\,dv$$

tends to $\frac{1}{2}\pi\psi(\mu,\nu)$ or to 0, according as (μ,ν) does or does not lie in q;* and so

$$\Sigma \mathrm{J}_q \rightarrow \pi\, \Sigma\, \psi(\mu,\nu). \tag{3.26}$$

The lemma follows from (3.22), (3.23) and (3.26).

3.3. In Lemma 4 we take $\psi = x - u^2 - v^2$, and we obtain

$$\mathrm{J} \rightarrow \pi\, \Sigma\,(x-\mu^2-\nu^2) = \pi \sum_{0 \leqq p < x} (x-p)\, r(p) = \pi \int_0^x \mathrm{A}(\xi)\, d\xi. \tag{3.31}$$

On the other hand, by (3.12),

$$\begin{aligned}\mathrm{J} &= \pi \iint_{\mathrm{K}} (x-u^2-v^2) \sum_{m,n} e^{-(m^2+n^2)\pi^2\delta^2} \cos 2m\pi u \cos 2n\pi v\, du\, dv \\ &= \pi \iint (x-u^2-v^2)\, du\, dv \\ &\qquad + \pi \sum_{m,n}{}' e^{-(m^2+n^2)\pi^2\delta^2} \iint \cos 2m\pi u \cos 2n\pi v\,(x-u^2-v^2)\, du\, dv.\dagger\end{aligned}$$

But

$$\iint \cos 2m\pi u \cos 2n\pi v\,(x-u^2-v^2)\, du\, dv = \frac{x\mathrm{J}_2\{2\pi\sqrt{(m^2+n^2)x}\}}{\pi(m^2+n^2)}$$

unless $m = 0$, $n = 0$, in which case its value is $\frac{1}{2}\pi x^2$.‡ Hence

$$\pi \int_0^x \mathrm{A}(\xi)\, d\xi = \lim_{\delta \to 0} \mathrm{J} = \lim_{\delta \to 0} \left\{\tfrac{1}{2}\pi^2 x^2 + x \sum_1^\infty \frac{r(\nu)}{\nu} \mathrm{J}_2(2\pi\sqrt{\nu x})\, e^{-\nu\pi^2\delta^2}\right\}.$$

The series is uniformly convergent for $\delta \geqq 0$, since $\mathrm{J}_2(2\pi\sqrt{\nu x}) = O(\nu^{-\frac{1}{4}})$. We may therefore put $\delta = 0$, when we obtain (1.22).

It is plain that, if we had taken $\psi = 1$, we should have obtained

$$\mathrm{P}(x) = \sqrt{x} \lim_{\delta \to 0} \sum_1^\infty \frac{r(\nu)}{\sqrt{\nu}} \mathrm{J}_1(2\pi\sqrt{\nu x})\, e^{-\nu\pi^2\delta^2};$$

the series (1.21), summed by an Abelian limit. We should naturally not be able to proceed to the limit under the sign of summation without some independent proof of the convergence of (1.21).

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* By a classical theorem of Weierstrass. See K. Weierstrass, "Über die analytische Darstellbarkeit sogenannter willkürlicher Functionen reeller Argumente," 'Berliner Sitzungsberichte,' pp. 633–639 and 789–805 (1885) (Werke, vol. 3, pp. 1–37); É. Borel, "Leçons sur les fonctions de variables réelles," ch. 4 (1905).

† The term by term integration is obviously trivial.

‡ See E. Landau, "Neue Untersuchungen über die Pfeiffer'sche Methode zur Abschätzung von Gitterpunktanzahlen," 'Wiener Berichte,' vol. 124, pp. 469–505 (1915) (Hilfssatz 6).

4. *Proof of* (1.21) *by real analysis.*

4.1. In this section we deduce (1.21) from (1.22). We assume concerning Bessel functions only the following propositions :*

$$J_0(0)=1,\quad J_1(t)\sim\tfrac12 t\quad (t\to 0),$$

$$\frac{d}{dt}\left\{\frac{J_h(l\sqrt{t})}{t^{\frac12 h}}\right\}=-\tfrac12 l\frac{J_{h+1}(l\sqrt{t})}{t^{\frac12(h+1)}},$$

$$\int_0^\infty J_2(Nt)\,J_3(t)\,dt=N^2\ (0<N<1),\quad =\tfrac12\ (N=1),\quad =0\ (N>1),$$

$$|J_h(t)|<\frac{K}{\sqrt{t}},\quad \left|J_h(t)-\sqrt{\frac{2}{\pi t}}\cos(t-\tfrac12 h\pi-\tfrac14)\right|<\frac{K}{t^{\frac32}}.$$

Here $t>0$, $l>0$, $h=0, 1, 2, 3$. The K's are absolute constants.

In what follows, x, a, α, β are positive ; the B's are positive and depend upon a only ; the L's are positive and depend upon α and β only ; and the M's are positive and depend upon x only.

4.2. LEMMA 5. *If* $w>0$, $N>a$, *then*

$$\left|\int_w^\infty J_2(Nt)\,J_3(t)\,dt+\frac{sgn\,(N-1)}{\pi\sqrt{N}}\int_{|N-1|w}^\infty\frac{\sin u}{u}\,du\right|<\frac{B}{w\sqrt{N}}. \qquad (4.21)$$

If in addition $|N-1|>a$, *then*

$$\left|\int_w^\infty J_2(Nt)\,J_3(t)\,dt\right|<\frac{B}{w\sqrt{N}}. \qquad (4.22)$$

We have

$$J_2(Nt)\,J_3(t)=-\frac{2}{\pi\sqrt{N}}\,\frac{\cos(Nt-\frac14\pi)\cos(t+\frac14\pi)}{t}+\phi(N,t), \qquad (4.23)$$

where

$$|\phi(N,t)|<K\left(\frac{1}{\sqrt{Nt}}\cdot\frac{1}{t^{\frac32}}+\frac{1}{(Nt)^{\frac32}}\cdot\frac{1}{\sqrt{t}}\right)<\frac{B}{t^2\sqrt{N}},$$

$$\left|\int_w^\infty \phi(N,t)\,dt\right|<\frac{B}{w\sqrt{N}}. \qquad (4.24)$$

Also

$$2\int_w^\infty\frac{\cos(Nt-\frac14\pi)\cos(t+\frac14\pi)}{t}\,dt=\int_w^\infty\frac{\cos(N+1)t}{t}\,dt+\int_w^\infty\frac{\sin(N-1)t}{t}\,dt, \qquad (4.25)$$

$$\left|\int_w^\infty\frac{\cos(N+1)t}{t}\,dt\right|=\left|\int_{w(N+1)}^\infty\frac{\cos u}{u}\,du\right|<\frac{K}{w}, \qquad (4.26)$$

$$\int_w^\infty\frac{\sin(N-1)t}{t}\,dt=sgn\,(N-1)\int_{|N-1|w}^\infty\frac{\sin u}{u}\,du,$$

$$\left|\int_w^\infty\frac{\sin(N-1)t}{t}\,dt\right|<\frac{B}{w}\quad (|N-1|>a). \qquad (4.27)$$

---

* Watson, pp. 16, 18, 199, 406.

The lemma follows from (4.23)—(4.27).

Lemma 6. *We have*

$$P_1(t) = O(t^{3/4}). \tag{4.28}$$

For, by (1.22),

$$|P_1(t)| < Kt \sum_1^\infty \frac{r(\nu)}{\nu} \frac{1}{(\nu t)^{1/4}} < Kt^{3/4} \quad (t \geqq 1).$$

4.3. **Theorem 1.** *If x and x_1 are positive, then*

$$\begin{aligned}\overline{P}(x) = \sqrt{x} \sum_{1 \leqq \nu \leqq x_1} \frac{r(\nu)}{\sqrt{\nu}} J_1(2\pi\sqrt{\nu x}) + J_0(2\pi\sqrt{xx_1}) \\ - \sqrt{\frac{x}{x_1}} P(x_1) J_1(2\pi\sqrt{xx_1}) - \frac{\pi x}{x_1} P_1(x_1) J_2(2\pi\sqrt{xx_1}) \\ + x \sum_1^x \frac{r(\nu)}{\nu} \int_{2\pi\sqrt{xx_1}}^x J_3(t) J_2\left(t\sqrt{\frac{\nu}{x}}\right) dt.\end{aligned} \tag{4.31}$$

It is convenient to regard $J_1(2\pi\sqrt{\nu x})/\sqrt{\nu}$ as meaning $\pi\sqrt{x}$ (its limit when $\nu \to 0$) when $\nu = 0$. This being so, we have

$$\begin{aligned}&\sqrt{x} \sum_{0 \leqq \nu \leqq x_1} \frac{r(\nu)}{\sqrt{\nu}} J_1(2\pi\sqrt{\nu x}) - \sqrt{\frac{x}{x_1}} P(x_1) J_1(2\pi\sqrt{xx_1}) + J_0(2\pi\sqrt{xx_1}) - 1 \\ &= -\sqrt{x} \sum_{0 \leqq \nu \leqq x_1} r(\nu) \left(\frac{J_1(2\pi\sqrt{xx_1})}{\sqrt{x_1}} - \frac{J_1(2\pi\sqrt{\nu x})}{\sqrt{\nu}} \right) \\ &\qquad + \pi x_1 \sqrt{x} \frac{J_1(2\pi\sqrt{xx_1})}{\sqrt{x_1}} + \int_0^{x_1} dJ_0(2\pi\sqrt{xt}) \\ &= -\sqrt{x} \sum_{0 \leqq \nu \leqq x_1} r(\nu) \int_\nu^{x_1} d\,\frac{J_1(2\pi\sqrt{xt})}{\sqrt{t}} \\ &\qquad + \pi\sqrt{x} \left(x_1 \frac{J_1(2\pi\sqrt{xx_1})}{\sqrt{x_1}} - \int_0^{x_1} \frac{J_1(2\pi\sqrt{xt})}{\sqrt{t}}\, dt \right) \\ &= -\sqrt{x} \int_0^{x_1} \sum_{0 \leqq \nu \leqq t} r(\nu)\, d\,\frac{J_1(2\pi\sqrt{xt})}{\sqrt{t}} + \pi\sqrt{x} \int_0^{x_1} t\, d\,\frac{J_1(2\pi\sqrt{xt})}{\sqrt{t}} \\ &= -\sqrt{x} \int_0^{x_1} P(t)\, d\,\frac{J_1(2\pi\sqrt{xt})}{\sqrt{t}} = \pi x \int_0^{x_1} P(t) \frac{J_2(2\pi\sqrt{xt})}{t}\, dt \\ &= \pi x P_1(x_1) \frac{J_2(2\pi\sqrt{xx_1})}{x_1} + \pi^2 x^{\frac{3}{2}} \int_0^{x_1} P_1(t) \frac{J_3(2\pi\sqrt{xt})}{t^{\frac{3}{2}}}\, dt.\end{aligned} \tag{4.32}$$

Also, by (1.22),

$$\pi^2 x^{\frac12}\int_0^{x_1} \mathrm{P}_1(t)\,\frac{\mathrm{J}_3(2\pi\sqrt{xt})}{t^{\frac32}}\,dt = \pi x^{\frac12}\sum_1^{\infty}\frac{r(\nu)}{\nu}\int_0^{x_1}\frac{\mathrm{J}_2(2\pi\sqrt{\nu t})\,\mathrm{J}_3(2\pi\sqrt{xt})}{\sqrt{t}}\,dt$$

$$= x\sum_1^{\infty}\frac{r(\nu)}{\nu}\int_0^{2\pi\sqrt{xx_1}}\mathrm{J}_2\left(t\sqrt{\frac{\nu}{x}}\right)\mathrm{J}_3(t)\,dt = x\sum_1^{\infty}\frac{r(\nu)}{\nu}\left(\int_0^{\infty}-\int_{2\pi\sqrt{xx_1}}^{\infty}\right)$$

$$= \overline{\mathrm{A}}(x) - 1 - x\sum_1^{\infty}\frac{r(\nu)}{\nu}\int_{2\pi\sqrt{xx_1}}^{\infty}\mathrm{J}_2\left(t\sqrt{\frac{\nu}{x}}\right)\mathrm{J}_3(t)\,dt. \tag{4.33}$$

Comparing (4.32) and (4.33) we obtain (4.31).

4.4. THEOREM 2. *If x is positive and fixed, and $\mathrm{P}(t) = O(t^{\theta})$, where $\theta > \frac14$,* then*

$$\sqrt{x}\sum_1^{m}\frac{r(\nu)}{\sqrt{\nu}}\mathrm{J}_1(2\pi\sqrt{\nu x}) = \overline{\mathrm{P}}(x) - \frac{\cos(2\pi\sqrt{mx}-\frac14\pi)}{\pi m^{\frac14}x^{\frac14}} + O(m^{-\frac14+\theta}). \tag{4.41}$$

Suppose that $0 < \alpha \leqq x \leqq \beta$,† $m > 0$. Then, by (4.31) and (4.28),

$$\left|\sqrt{x}\sum_1^{m}\frac{r(\nu)}{\sqrt{\nu}}\mathrm{J}_1(2\pi\sqrt{\nu x}) - \overline{\mathrm{P}}(x) + \frac{\cos(2\pi\sqrt{mx}-\frac14\pi)}{\pi m^{\frac14}x^{\frac14}}\right.$$

$$\left. + x\sum_1^{\infty}\frac{r(\nu)}{\nu}\int_{2\pi\sqrt{mx}}^{\infty}\mathrm{J}_2\left(t\sqrt{\frac{\nu}{x}}\right)\mathrm{J}_3(t)\,dt\right|$$

$$= \left|\frac{\cos(2\pi\sqrt{mx}-\frac14\pi)}{\pi m^{\frac14}x^{\frac14}} - \mathrm{J}_0(2\pi\sqrt{mx}) + \sqrt{\frac{x}{m}}\,\mathrm{P}(m)\,\mathrm{J}_1(2\pi\sqrt{mx})\right.$$

$$\left. + \frac{\pi x}{m}\mathrm{P}_1(m)\,\mathrm{J}_2(2\pi\sqrt{mx})\right|$$

$$< \mathrm{L}(m^{-\frac34} + m^{-\frac12}\,.\,m^{\theta}\,.\,m^{-\frac14} + m^{-1}\,.\,m^{\frac34}\,.\,m^{-\frac14}) < \mathrm{L}m^{\theta-\frac14}. \tag{4.42}$$

Now $\sqrt{\nu/x} > \mathrm{M}$; and $|\sqrt{\nu/x}-1| > \mathrm{M}$ unless $x = \nu$. Hence, whether x be integral or not,‡

$$\left|\int_{2\pi\sqrt{mx}}^{\infty}\mathrm{J}_2\left(t\sqrt{\frac{\nu}{x}}\right)\mathrm{J}_3(t)\,dt\right| < \frac{\mathrm{M}}{\sqrt{mx}\,(\nu/x)^{\frac34}} < \frac{\mathrm{M}}{\sqrt{m}\,\nu^{\frac34}}; \tag{4.43}$$

and so

$$\left|x\sum_1^{\infty}\frac{r(\nu)}{\nu}\int_{2\pi\sqrt{mx}}^{\infty}\mathrm{J}_2\left(t\sqrt{\frac{\nu}{x}}\right)\mathrm{J}_3(t)\,dt\right| < \frac{\mathrm{M}}{\sqrt{m}}\sum_1^{\infty}\frac{r(\nu)}{\nu^{\frac74}} < \frac{\mathrm{M}}{\sqrt{m}} < \mathrm{M}m^{\theta-\frac14}. \tag{4.44}$$

Combining (4.42) and (4.44), we obtain (4.41).

---

* In fact, if $\mathrm{P}(t) = O(t^{\theta})$, θ is necessarily greater than $\frac14$. That θ cannot be less than $\frac14$ follows from the investigations of Hardy and Landau, quoted on p. 245 (f.n. * and †); and that it cannot be equal to $\frac14$ from a later investigation of Hardy (see G. H. Hardy, "On Dirichlet's divisor problem," 'Proc. London Math. Soc.' (2), vol. 15, pp. 1–25 (23) (1916)).

† With a view to the sequel.

‡ We use (4.22) unless $x = \nu$, N = 1, and in that case (4.21), in which $\mathrm{sgn}\,(\mathrm{N}-1) = 0$.

It is trivial that $\theta \leqq \frac{1}{2}$. Hence, for fixed x,

$$\sqrt{x}\sum_{1}^{m}\frac{r(\nu)}{\sqrt{\nu}}J_1(2\pi\sqrt{\nu x}) = \overline{P}(x) + O(m^{-\frac{1}{4}}).$$

This completes the proof of (1.21) by our present method.

4.5. THEOREM 3. *If* $0 < \alpha \leqq x \leqq \beta$, *and* g *is the positive integer nearest to* x,* *then*

$$\left|\sqrt{x}\sum_{1}^{m}\frac{r(\nu)}{\sqrt{\nu}}J_1(2\pi\sqrt{\nu x}) - \overline{P}(x) + \frac{\cos(2\pi\sqrt{mx}-\frac{1}{4}\pi)}{\pi m^{\frac{1}{4}}x^{\frac{1}{4}}}\right.$$
$$\left. -\frac{r(g)}{\pi}\left(\frac{x}{g}\right)^{\frac{1}{4}} sgn\,(g-x)\int_{2\pi|\sqrt{g}-\sqrt{x}|\sqrt{m}}^{\infty}\frac{\sin u}{u}\,du\right| < Lm^{\theta-\frac{3}{4}}. \tag{4.51}$$

If $\nu \neq g$, $\sqrt{\nu/x}$ and $|\sqrt{\nu/x}-1|$ are each greater than L, and (4.43) holds with L in the place of M. Hence, as in the proof of (4.41),

$$\left|x\sum_{1}^{\infty}{}'\frac{r(\nu)}{\nu}\int_{2\pi\sqrt{mx}}^{\infty}J_2\left(t\sqrt{\frac{\nu}{x}}\right)J_3(t)\,dt\right| < \frac{L}{\sqrt{m}}, \tag{4.52}$$

the dash indicating that $\nu = g$ is excluded. On the other hand, since $\sqrt{g/x} > L$, we have, by (4.21),

$$\left|x\frac{r(g)}{g}\int_{2\pi\sqrt{mx}}^{\infty}J_2\left(t\sqrt{\frac{g}{x}}\right)J_3(t)\,dt\right.$$
$$\left.+\frac{r(g)}{\pi}\left(\frac{x}{g}\right)^{\frac{1}{4}} sgn\,(g-x)\int_{2\pi|\sqrt{g}-\sqrt{x}|\sqrt{m}}^{\infty}\frac{\sin u}{u}\,du\right| < \frac{L}{\sqrt{mx}\,(g/x)^{\frac{1}{4}}} < \frac{L}{\sqrt{m}}. \tag{4.53}$$

Combining (4.52) and (4.53) with (4.42), we obtain (4.51). It will be observed that

$$\left|\sum_{1}^{m}\frac{r(\nu)}{\sqrt{\nu}}J_1(2\pi\sqrt{\nu x})\right| < L.$$

If (α, β) contains no integer, $2\pi|\sqrt{g}-\sqrt{x}| > L$; so that

$$\left|\sqrt{x}\sum_{1}^{m}\frac{r(\nu)}{\sqrt{\nu}}J_1(2\pi\sqrt{\nu x}) - P(x) + \frac{\cos(2\pi\sqrt{mx}-\frac{1}{4}\pi)}{\pi m^{\frac{1}{4}}x^{\frac{1}{4}}}\right| < Lm^{\theta-\frac{3}{4}},$$

$$\left|\sqrt{x}\sum_{1}^{m}\frac{r(\nu)}{\sqrt{\nu}}J_1(2\pi\sqrt{\nu x}) - P(x)\right| < Lm^{-\frac{1}{4}}.$$

Thus the convergence of (1.21) is uniform in any such interval. The formula (4.51) also exhibits the Gibbs phenomenon of the series, which has the magnitude stated in 2.4.

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[*] If $x = m + \frac{1}{2}$, where m is a positive integer, then g may be either m or $m + 1$.

The Doublet Separation of the Balmer Lines.

By G. M. SHRUM, M.A., University of Toronto.

(Communicated by Prof. J. C. McLennan, F.R.S. Received December 8, 1923.)

[PLATE 3.]

Introduction.

According to the Bohr Theory the hydrogen atom consists of an electron in circular or elliptical motion about a positively charged nucleus. The steady states are defined by discrete values of the angular momentum and, in the case of elliptical motion, the eccentricities of the ellipses are limited to certain definite values. Sommerfeld, by an extension of Bohr's theory involving quantising both angular and radial momenta, has established the formula

$$\gamma = \frac{2\pi^2 m E^2 e^2}{h^3}\left[\frac{1}{(T'_1 + T'_2)^2} - \frac{1}{(T_1 + T_2)^2}\right]$$

for the spectral series emitted by a system consisting of a nucleus with charge $+ E$ and an electron with charge $- e$. This is the familiar formula in which terms are included corresponding to elliptical as well as to circular motion for the revolving electron.

By the theory of relativity it can be shown that the mass of an electron in the elliptical orbit is not the same as its mass in the circular orbit, but that it depends on the velocity v, thus $m = m_0 (\sqrt{1 - \beta^2})^{-\frac{1}{2}}$, where $\beta = \frac{v}{c}$ and m_0 is the mass of the slow-moving electron. From a mathematical standpoint for a slow-moving electron we may consider the path as an ellipse with slowly moving perihelion. Applying this relativity correction, the above formula becomes

$$\gamma = NZ^2\Big[\frac{1}{(T'_1 + T'_2)^2} + \frac{\alpha^2 Z^2}{(T'_1 + T'_2)^4} \quad + \frac{T'_2}{T'_1}\Big) + \cdots$$

$$- \frac{1}{(T_1 + T_2)^2} - \frac{\alpha^2 Z^2}{(T_1 + T_2)^4}\left(\tfrac{1}{4} + \frac{T_2}{T_1}\right) - \cdots\Big]$$

where $$N = \frac{2\pi^2 m_0 e^4}{h^3}, \qquad \alpha = \frac{2\pi e^2}{hc},$$

and Z = Atomic Number.

For hydrogen we may put $E = e$. The Balmer series involves a two-quantum orbit for the final state, and thus if we put $T'_1 + T'_2 = 2$ the formula becomes

$$\gamma = N'\left(\tfrac{1}{4} - \frac{1}{n^2}\right) + N_H \frac{\pi^2 e^4}{h^2 c^2}\left(\frac{T'_2}{4T_1} - \frac{4T_2}{T_1 n^4}\right) + \ldots$$

where

$$N' = N_H\left[1 + \frac{\pi^2 e^4}{h^2 c^2}\left(\tfrac{1}{4} + \frac{1}{n^2}\right) + \ldots\right].$$

Using this equation, Sommerfeld* has shown that each member of the doublet H_α should consist of a close triplet, each member of H_β of a close quartette, each member of H_γ of a close quintette, etc. He has also pointed out that for the two-quantum orbit, *i.e.*, $T'_1 + T'_2 = 2$, there are two possibilities, either $T'_1 = 1$ and $T'_2 = 1$, or $T'_1 = 2$ and $T'_2 = 0$. The value $T'_1 = 0$ is barred, as it results in a linear motion through the nucleus. Thus the frequency for an electron falling into the circular orbit may be expressed as follows :—

$$\gamma = N'\left(\tfrac{1}{4} - \frac{1}{n^2}\right) - N_H \frac{\pi^2 e^4}{h^2 c^2} \cdot \frac{4T_2}{n^4 T_1} + \ldots,$$

and for one falling into the elliptical orbit

$$\gamma = N'\left(\tfrac{1}{4} - \frac{1}{n^2}\right) - N_H \frac{\pi^2 e^4}{h^2 c^2}\left(\frac{4T_2}{n^4 T_1} - \tfrac{1}{4}\right) + \ldots.$$

The frequency difference $d\gamma$ of the doublets of the Balmer series is thus shown to be constant, and given by

$$d\gamma = \tfrac{1}{4}\frac{\pi^2 e^4}{h^2 c^2} N_H = 0 \cdot 365 \text{ cm.}^{-1}.$$

It has been shown that in the case of H_α H_β and H_γ the calculated distribution and intensities of the fine structural components are such that in actual determinations of the doublet separations, values somewhat less than $0 \cdot 365$ cm.$^{-1}$ should be obtained. Thus in proceeding from H_α to the higher members of the series, it would be expected, on the basis of the theory, to obtain for the doublet separation values slightly less for H_α, but rapidly increasing to $0 \cdot 365$ cm.$^{-1}$ for H_δ and remaining constant for the higher members of the series.

Owing to the small mass of the hydrogen atom, a direct proof of Sommerfeld's theory by observation of the hydrogen lines is a somewhat difficult undertaking. As Foote and Mohler† have pointed out, the entire fine structure of the H_α

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* Sommerfeld, 'Atombau und Spektrallinien,' p. 344.

† Foote and Mohler, 'The Origin of Spectra,' p. 27.

line, as given by Sommerfeld, would cover a spectral range of only 0·2 Å.U. The width of a spectral line, assuming it to be accounted for wholly by the Doppler-Fizeau effect, may be shown* to be

$$\Delta = 0{\cdot}86 \,.\, 10^{-6}\, \lambda \sqrt{T/M}$$

where M is the molecular weight and T the absolute temperature of the radiating gas. Since M = 1 for hydrogen, it is readily apparent that the Doppler effect will be quite pronounced and tend to mask any phenomena due to the fine structure. Even with the discharge tube immersed in liquid air, it can be shown that the theoretical width of each component of H_α should be 0·051 A. Merton† has drawn attention to the effect of an electric field on the radiating particle, either imposed by the electrodes of the tube or the field due to the neighbouring atoms, as suggested by Stark.‡ Owing to these difficulties, the Sommerfeld theory has not as yet been confirmed by a direct observation of the fine structure of the hydrogen lines.

The helium atom, however, is four times as heavy as that of hydrogen, while the nuclear discharge is double ; so in consequence the separation of the doublets should be, according to the theory, 16 times as great. Paschen,§ by studying the spectrum of the ionised helium atom, found a good agreement between observation and theory. In applying these results to hydrogen he deduced that the separation for the hydrogen doublets should be given by $d\nu = 0{\cdot}365 \pm 0{\cdot}0045$ cm.$^{-1}$, exactly as Sommerfeld had predicted theoretically.

However, the main criticism of Sommerfeld's theory has not been that Paschen failed to find the lines exactly as predicted for the univalent helium atom, nor that all investigators have failed in their attempts to observe the fine structure of the hydrogen lines, but rather that there has been no agreement between the observed values of the doublet separation of the Balmer series and the constant value deduced theoretically by Sommerfeld. However, it should be noted here that the agreement among the observed values themselves is not better than the agreement between the observed and theoretical values.

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* Nagaoka, 'Proc. Math. Phys. Soc., Tokyo,' pp. 237–43 (1915) ; Lord Rayleigh, 'Phil. Mag.,' vol. 2, p. 274 (1915).

† Merton, 'Roy. Soc. Proc.,' A, vol. 92, p. 322 (1915).

‡ Stark, 'Elektrische Spektralanalyse Chemischer Atome' (1914).

§ Paschen, 'Ann. der Phys.,' vol. 1, p. 933 (1916).

Some of the experimental values are as follows :—

H_α.	$\Delta\lambda$ (Å.U).	$\Delta\gamma$ (cm.$^{-1}$).
Michelson and Morley (1)	0·11	0·253
Ebert (2)	0·132	0·307
Michelson (3)	0·14	0·323
Houstoun (4)	0·065	0·153
Fabry and Buisson (5)	0·132	0·306
Meissner (6)	0·124	0·288
Merton and Nicholson (7)	0·132	0·306
Merton (8)	0·145	0·34
McLennan and Lowe (9)	0·154	0·36
Gehreke and Lau (10)	0·126	0·293
Geddes (11)	0·146	0·34
Oldenberg (12)	0·450	0·35

(1) Michelson and Morley, 'Phil. Mag.,' vol. 24, p. 46 (1887).
(2) Ebert, 'Wied. Ann. (N.P.),' vol. 43, p. 800 (1891).
(3) Michelson, 'Bur. Int. des Poids et Mesures,' vol. 11, p. 139 (1895).
(4) Houstoun, 'Phil. Mag.,' vol. 7, p. 456 (1904).
(5) Fabry and Buisson, 'C.R.,' vol. 154, p. 1501 (1912).
(7) Merton and Nicholson, 'Roy. Soc. Proc.,' A, vol. 93, p. 28 (1917).
(6) Meissner, *see* Paschen, 'Ann der Phys.,' vol. 50, p. 933 (1916).
(8) Merton, 'Roy. Soc. Proc.,' A, vol. 97, p. 307 (1920).
(9) McLennan and Lowe, 'Roy. Soc. Proc.,' A, vol. 100.
(10) Gehrcke and Lau, 'Phys. Zeit.,' vol. 21, p. 634 (1920).
(11) Geddes, 'Roy. Soc. Proc.,' Edinburgh, vol. xliii, p. 37 (1922).
(12) Oldenberg, 'Ann. der Phys.,' vol. 67, p. 253 (1922).

H_β.	$\Delta\lambda$ A.	$\Delta\gamma$ cm.$^{-1}$.
Michelson	0·08	0·33
Merton and Nicholson	0·033	0·14
Merton	0·093	0·39
Gehrcke and Lau	0·0695	0·294
McLennan and Lowe	0·085	0·36
Geddes	0·078	0·33

H_γ.	$\Delta\lambda$ A.	$\Delta\gamma$ cm.$^{-1}$.
Gehrcke and Lau	0·058	0·31
McLennan and Lowe	0·062	0·33
Wood (*)	0·058	0·31

H_δ.	$\Delta\lambda$ A.	$\Delta\gamma$ cm.$^{-1}$.
Gehrcke and Lau	0·043	0·26
McLennan and Lowe	0·049	0·29

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* Wood, 'Phil. Mag.,' p. 538, Sept., 1922.

On the whole, it will be seen that the values obtained are somewhat less than those demanded by the theory. In the case of some of the observations, the values indicate a steady decrease for the frequency differences as one passes to the higher members of the series. This would indicate that the Balmer series should be classified as a principal, rather than a subordinate, series.

This lack of agreement among the results of different observers has brought out much theoretical speculation, and many very refined experimental methods have been developed in the search for evidence that would lead to a confirmation or rejection of the Sommerfeld theory. Stark* says that, according to the best experimental values both in hydrogen and helium, the Sommerfeld theory of the fine structure of the series lines will not satisfy the experimental results. He adds that, since the theory is based upon the Bohr quantum theory of the emission of spectral lines, together with an extension due to the special theory of relativity, and since the latter can be verified by many independent methods, therefore the former theory must be false.

It is evident that much of the variation in the results must be attributed to the difficulty in measuring the separation of the wide and more or less diffuse components of the doublets. Further, both Merton and Gehrcke and Lau† have shown that it is possible to get various values for the separation depending upon the conditions under which the tube is excited. From this evidence it is not unreasonable to expect that the lines may be complex, consisting perhaps of three or more components, and quite in harmony with Sommerfeld's theoretical deductions.

The author, under very favourable conditions, has succeeded in photographing the doublet separations for the first five members of the Balmer series. In this work an arrangement was perfected whereby, when liquid air was used to reduce the Doppler effect, only light from the cooled section of the tube was allowed to fall upon the interference spectrograph. By this means very sharp photographs were obtained, and from these it was found possible to make a very precise determination of the doublet separation. It will suffice to state here that these results show that the doublet separation is not only constant but has a value almost in exact agreement with the theory of Sommerfeld.

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* Stark, 'Jahrbuch der Radioaktivität und Elektronik,' vol. 17 (1920).

† *Loc. cit.*

Apparatus.

The discharge tube (*see* Fig. 1) was made from clear fused quartz, and was somewhat similar to that used by Wood* in photographing the higher members of the Balmer series. The central part of the tube consisted of a tube of quartz 1·2 cm. in diameter and 50 cm. long. A quartz window was sealed in either end of this tube, and two similar tubes bearing the electrodes were joined to it as shown in the diagram. The central tube was surrounded by two concentric quartz tubes, 3·8 cm. and 5 cm. in diameter. These were drawn down at the ends and sealed to the central tube. The closed space between these two tubes, when thoroughly exhausted and sealed, served to form a vacuum container suitable for liquid air or liquid hydrogen. It was found that when sound and durable seals had once been effected no difficulty was experienced from unequal contraction at the low temperatures. It is evident that the coefficient of expansion for quartz, although very small at ordinary temperatures, must fall off very rapidly for low temperatures. During the operation only the ends of the outer tube became coated with frost, and the extension provided for the windows insured that they remained clear at all times. This type of tube permitted a very economical use of the liquid air and liquid hydrogen, and thus it was possible to make comparatively extended observations at these low temperatures. The detailed drawing shows clearly the design of the electrodes and the method employed for sealing in the tungsten leads. The aluminium pieces were quite heavy, and were turned from a solid aluminium rod. This particular design prevented local heating effects in the

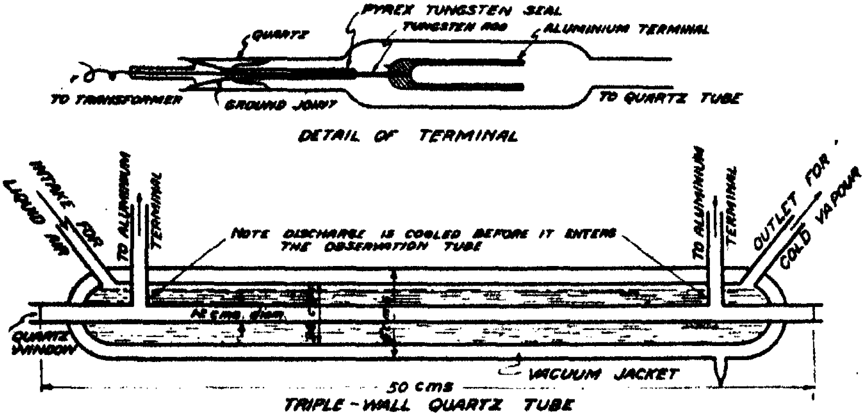

Fig. 1.

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* Wood, 'Roy. Soc. Proc.,' A, vol. 97, p. 455 (1920).

surrounding quartz tube; this was of particular importance when observations were made on the higher members of the series. In order to bring out these lines the tube was operated at very low pressures and high current values, and consequently the heating effect was considerable.

The hydrogen was introduced from a storage tank by means of a delicate micrometer valve, as shown in Fig. 2. It was carefully dried and purified by passing it over a number of tubes of cocoanut charcoal at liquid-air temperature.

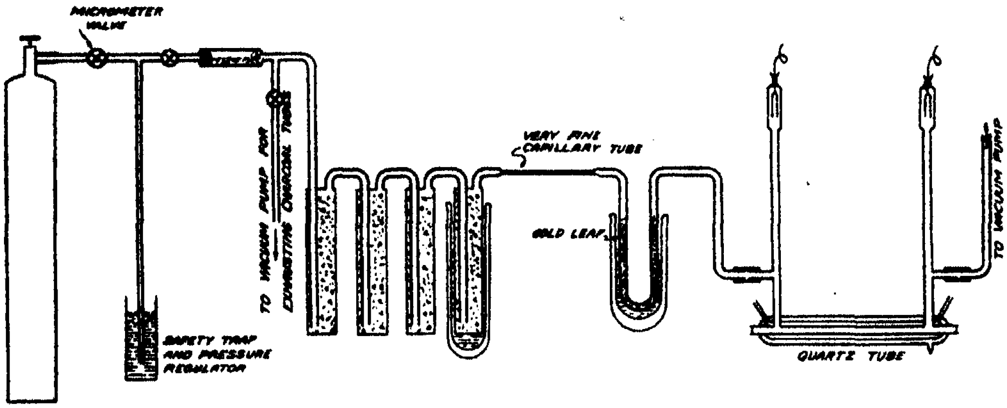
MICROMETER VALVE
TO VACUUM PUMP FOR EXHAUSTING CHARCOAL TUBES
SAFETY TRAP AND PRESSURE REGULATOR
VERY FINE CAPILLARY TUBE
GOLD LEAF
QUARTZ TUBE
TO VACUUM PUMP

FIG. 2.

The discharge tube was protected from mercury vapour by means of two U-tubes filled with gold foil, and immersed in liquid air. These were placed in the gas cycle on either side of the tube. A Gaede rotary mercury pump was attached to the outlet of the discharge tube, as indicated in Fig. 2, and was kept continuously in operation whenever the tube was in use. Several methods of exciting the tube were tried, and the best results were obtained with a Wappler 100,000 volt X-ray transformer. The potential difference applied across the tube was varied by introducing resistance into the primary circuit. The transformer was operated on a 200-volt 25-cycle circuit, and the average current maintained in the primary was 20 to 30 ampères.

The tube was mounted so that the light from both ends could be examined simultaneously. During the operation of the tube a Hilger constant-deviation spectrograph was used to record, photographically, the purity of the gas and the relative intensities of the Balmer and secondary spectra. The light from the other end of the tube was examined by means of a Lummer plate, for which the optical data were the following:—

Optical Data of Lummer Plate.

l = 13 cm.

d = 0·448 cm.

$\frac{d\mu}{d\lambda}$ for H_α = − 324 cm.$^{-1}$.

H_β = −716 ,,

H_γ = −960 ,,

H_δ = −1150 ,,

H_ϵ = −1493 ,,

$\Delta\lambda m$ for H_α = 0·4159 A.

H_β = 0·2224 ,,

H_γ = 0·1755 ,,

H_δ = 0·1550 ,,

H_ϵ = 0·1518 ,,

Refractive Indices.

λ(A)	μ
6563·045	1·50746
5896·155 5890·186	1·50990
4861·49	1·51560
4308·08	1·52025

The dispersion formula used

$$\mu 1\cdot491324 + \frac{82\cdot2922}{\lambda - 1463\cdot17}$$

$$\mu\ 1\cdot494199 + \frac{69\cdot3239}{\lambda - 2089\cdot47}$$

The Lummer plate was mounted with its plane parallel faces vertical. The light used was that which issued axially from the central portion of the discharge tube. The mounting was arranged so that the position of the plate could be adjusted by means of graduated micrometer screws. By this arrangement a record of the various positions of the plate could be tabulated and a corresponding series of photographs taken.

Qualitative Observations.

At ordinary temperatures and with pure hydrogen it was found, as Wood* has observed, that the transfer of energy from the secondary to the primary spectrum behaved very capriciously. Photographs showed that a great part of the energy of the discharge was represented as secondary spectrum. Observations in agreement with those of Merton and Wood were made, showing that the presence of water vapour was favourable to the production of the Balmer series with a corresponding decrease in intensity of the secondary spectrum.

It is now generally conceded that the Balmer series is produced by radiations from atomic hydrogen, while the secondary spectrum is due to the molecular formation. Wood has suggested that the potential applied to the tube is always sufficient to dissociate the hydrogen, but that the walls of the tube and the electrodes act as a catalyser, and almost instantaneously change the atomic hydrogen back into molecular hydrogen.

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* *Loc. cit.*

The general theory is that water vapour acts as a poison to the catalytic action of the walls of the tube. However, at the temperatures for which water vapour could be used for the above purpose, the hydrogen doublets appeared so diffuse, owing to the Doppler effect, enhanced perhaps by the Stark effect, that no measurements on the separation were attempted. In order to reduce the Doppler effect, the central discharge tube was surrounded with liquid air. At this temperature, as Wood and Merton have also observed, nearly all the energy of the discharge comes out in the secondary spectrum. Only the H_α and H_β lines appeared with sufficient intensity to be photographed as a Lummer plate pattern. The other lines of the series were lost in the practically continuous background due to the secondary spectrum.

The solution of the problem looked rather hopeless at the start, for it seemed that the devices used by Wood at ordinary temperatures, coupled with different methods of electrical excitation, variation of gas pressure, and many different methods of operation, would not transfer the maximum energy of the discharge into the Balmer series. The catalytic action of the walls of the tube seemed to be enhanced at the temperature of liquid air, and after many attempts to destroy it, the following method was adopted with considerable success :—

The central tube, after it had been thoroughly cleaned with hot chromic acid, and protected from mercury vapour as previously described, was cooled to − 190° C. by means of liquid air. Hydrogen containing a small percentage of air and at a pressure of about 5 mm. of mercury, was then passed through the tube. This impure gas was excited intermittently, by the discharge from the transformer, for a period varying from one to two hours. This insured that a very thin and even coating of water vapour was frozen on the inner walls of the tube. This layer of ice, together with the absorbed nitrogen, seemed to shield the atomic hydrogen from the catalytic action of the quartz walls. After this treatment, and while still at − 190° C., the discharge tube and connecting apparatus were thoroughly exhausted, and pure hydrogen was introduced into the system. When the tube was subsequently excited, even with moderate currents, providing the temperature had been maintained at − 190° C. in the interval, the secondary spectrum appeared only near the electrodes and in the warmer sections of the discharge tube. When the light from the cooled section of the tube was examined through a direct-vision spectrograph, the Balmer series appeared with great brilliancy against a practically black background. It required considerable practice in developing the technique of operating the tube before the secondary spectrum was so eliminated.

As is evident from Plate 3 the intensity of the secondary spectrum was not zero, but it was so small that no difficulty was experienced in isolating and photographing the Lummer plate patterns of the first five lines of the Balmer series. Spectra 2, 3, 4, 5, and 6 show the photographs of the Lummer plate patterns for the respective lines. The lines were comparatively sharp, and very little difficulty was experienced in measuring the doublet separations.

Many attempts were made to obtain the pattern for the sixth line of the series, but the results were always negative or doubtful, and no reliable measurements were obtained from them. It was comparatively easy to photograph H_ϵ, as it could be readily isolated by taking a series of photographs, starting with H_δ, which is in the visible region, and working towards the ultra-violet. A small camera requiring a short exposure was used to make a rough adjustment of the Lummer plate, and then with an exposure of from five to six hours with a larger camera, plates were obtained with sufficient density to give reliable measurements. The sixth line has only one-sixtieth of the intensity of the H_α line, and as it lies relatively close to H_ϵ and has a much smaller intensity, it was not possible to obtain a sufficient density on the photographs of the Lummer plate pattern.

Attempts were made to get evidence of the fine structure of the lines, and with this end in view the tube was cooled with liquid hydrogen. At this temperature the energy again shifted to the secondary spectrum and the intensity of the Balmer lines decreased in proportion. Lummer plate photographs with the tube at this temperature were attempted, but they were not dense enough to be reproduced. The lines, however, were observed very closely, and as in all the previous cases, no evidence of any fine structure was noted. This seems to be in agreement with the work of Oldenberg.* The satellites as observed by McLennan and Lowe and later by Geddes must therefore be attributable to the lines from the nitrogen or the secondary spectrum of hydrogen. These spectra were very intense in their photographs, as compared with the Balmer series, and it is possible that lines of an unknown origin may have appeared in the Lummer plate pattern of the Balmer lines.

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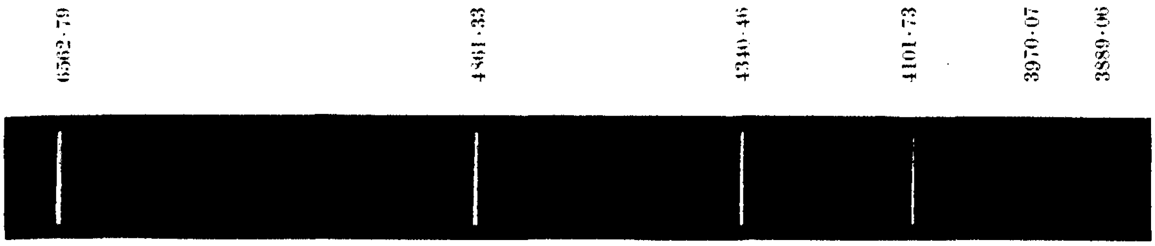
* Oldenberg, 'Ann. der Phys.,' vol. 67, p. 253 (1922).



1

2

H_α λ = 6562·79 Å.U.

3

H_β λ = 4861·33 Å.U.

4

H_γ λ = 4340·46 Å.U.

5

H_δ λ = 4101·73 Å.U.

6

H_ϵ λ = 3970·07 Å.U.

Quantitative Results.

In measuring the plates a Toepler comparator was used. The measurements were made from the edges as well as the centre of the lines in the photographs, and the apparent optical centre was taken to correspond with the line of maximum density on the plate.

The readings from the various plates were taken as the average of three complete sets, each consisting of three settings on each line. It was found necessary to reduce the current considerably in order to get sharp doublets for the H_α line, while the conditions for the other plates were always adjusted so as to give the maximum intensity for the line under examination.

The results of the measurements were as follows :—

a	*b*	*c*	*d*	
Line.	Wave-length in A.	Separation of the Components.		Probable Error.
		$d\lambda$.	$d\gamma$.	
H	6562·79	0·143 A	0·33 cm.$^{-1}$	±2·02
H	4861·33	0·085 ,,	0·36 ,,	±0·01
H	4340·46	0·070 ,,	0·37 ,,	±0·02
H	4101·73	0·061 ,,	0·36 ,,	±0·02
H	3970·07	0·055 ,,	0·35 ,,	±0·02

Summary of Results.

1. The doublet separations of the first five lines of the Balmer series have been determined and found to be almost in exact quantitative agreement with the theory of Sommerfeld.

2. A method has been described whereby the intensity of the Balmer lines relatively to the secondary spectrum may be increased many times, even when the discharge tube is at liquid-air temperatures.

3. No evidence of the fine structure was observed even under very favourable conditions.

4. The spectrum of pure hydrogen was studied when the discharge tube was at — 252° C. Evidence has been deduced to show that at this temperature the greater part of the gas is in the molecular condition.

Conclusions.

While it has been shown that a remarkable confirmation of Sommerfeld's theory has been obtained indirectly from Paschen's investigation of the structure of a number of wave-lengths in the spectrum of helium, and while it has been shown that the L series of the Röntgen spectra of the elements consists of doublets with a constant separation between the components of approximately 0·365 cm.$^{-1}$, the present values for the doublet separations of the Balmer lines represent the first direct proof of the theory in so far as the atoms of hydrogen are concerned.

Acknowledgments.

The author wishes to thank all those who have so materially assisted in this work, and in particular Professor J. C. McLennan, who suggested the problem and placed at the author's disposal all the necessary equipment. Much credit is also due to Mr. Chappell, who so patiently and skilfully constructed the triple-wall quartz tube.

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The Determination of Coefficients of Diffusion in Gels by means of Chemical Analysis, and a Comparison of Results obtained with those yielded by the Indicator Method.

By Charles E. T. Mann, B.Sc. (Wantage Hall Senior Scholar), University College, Reading.

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The first determination of the coefficient of diffusion of an electrolyte in a gel appears to have been made by Öholm (8) who calculated the coefficient of diffusion of potassium chloride in gels of gelatin of various concentrations, from the results of the chemical analysis of four successive layers of a cylinder of the gel, into which diffusion of the salt from a normal solution had proceeded.

Apart from these determinations of Öholm the only measurements of the coefficients of diffusion in gels are those made by Stiles and Adair (1, 9, 10 and 11) by means of the indicator method.

The following investigation was undertaken for the Department of Scientific and Industrial Research, with the object of obtaining, by a method based on chemical analysis, results directly comparable with the coefficients of diffusion of the various chlorides investigated by the indicator method. The work was carried out in the Botanical Department of University College, Reading, under the supervision of Professor Stiles.

Fick's law defines the coefficient of diffusion as D in the equation

$$dQ = -DA\frac{\partial c}{\partial x}dt \tag{1}$$

where dQ is the quantity of solute diffusing through a cylinder of cross-section A in the time dt at a point x where the concentration gradient is $\partial c/\partial x$. The minus sign indicates diffusion of the solute in the direction of decreasing concentration.

From this equation is obtained (6) the reduced equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{2}$$

which is analogous to Fourier's expression for the flow of heat and has different solutions according to the experimental conditions.

When a cylindrical tube of gel is immersed with one end in a vessel containing a solution of the salt, if the quantity of solution is large, in a tube so long as to be practically infinite, so far as the time of an ordinary experiment is concerned concentration at one end will be zero and at the other constant. Under these conditions the solution of the differential equation on the assumption that D is constant is as follows (*see, e.g.*, Lewis (6)):

$$C = C_0\left(1 - \frac{2}{\sqrt{\pi}}\int_0^q e^{-q^2}\,dq\right) \tag{3}$$

where C is the concentration after a time t at a point distant x from the surface separating salt and gel, and where C_0 is the original concentration of the diffusing salt and $q = \frac{x}{2\sqrt{Dt}}$.

Values of $I = \frac{2}{\sqrt{\pi}}\int_0^q e^{-q^2}dq$ for different values of q can be obtained from tables of the probability integral. As in the experiments described in this paper the initial concentration throughout the investigation was normal in each experiment, if C is measured in normalities,

$$C = 1 - I$$

whence the value of q is readily obtained and

$$D = \frac{x^2}{4\,(q^2)\,t}.$$

Method.

The experimental procedure was briefly as follows :—Tubes of hard glass of uniform bore were filled with a 2 per cent. agar-agar gel into which diffusion from a normal solution was allowed to proceed over a definite period. On removal sections of the gel were taken at definite levels and the concentration of chloride estimated by titration with 0·1 N silver nitrate.

Tubes varying in bore from 6 to 10 mm. and approximately 30 cm. long were carefully selected. One end of each was ground perfectly square on a fine carborundum stone and washed with xylol to remove oil after grinding. The ground tubes were then well washed in a cleaning solution consisting of 1 part of potassium bichromate, 5 parts of pure sulphuric acid and 10 parts of water. After soaking over-night in this solution the tubes were removed to distilled water. It was necessary to graduate each tube and the calibration was performed by the use of an accurate burette. Each tube was covered, over a distance of about 12 cm. from the ground end, with a thin coat of paraffin wax, the unground end being fitted with a waxed cylindrical cork. A distance of 10 cms. was accurately measured along the waxed surface and marked with a fine needle in the wax. Distilled water was now run in to the level of the lower mark, and the volume of the marked region was then obtained by filling from a burette. The volume obtained per centimetre length of tubing was scratched on the waxed surface and etched by painting with hydrofluoric acid. After removal of the wax the tubes were washed in hot distilled water and dried in a steam oven.

Certain precautions were observed in the preparation of the gel. Shred agar-agar was used and the gel was made up by weight, 1,000 gms. of gel containing 20 gms. of agar-agar. The first gel prepared appeared somewhat turbid and apparently contained small quantities of solid impurity. A sample was filtered, using a filter pump, and the amount of residue determined by weighing. The percentage of impurity thus obtained was so low (0·02 per cent.) that it appeared to be unnecessary to filter the whole. The error introduced by evaporation in filtering a large volume of gel, which must of necessity be almost at the boiling point, would be considerably greater. It was found that by heating the gel gently over a water-bath the bulk of the apparent impurities settled in about 20 minutes. An allowance based on the impurity found was made in weighing the agar-agar. The prepared gel was tested for chlorides using 0·1 normal silver nitrate and exhibited only the faintest trace of chloride.

In filling the tubes it is essential that the gel should adhere closely to the wall of the tube, and to ensure this the following method was found most suitable.

The prepared tubes were firmly bound in bundles of 10 and placed in a cylindrical vessel of suitable dimensions with corked ends resting on the bottom. A stout glass rod was put in alongside the bundle. The hot gel was then poured into the tubes and allowed to overflow, filling the containing vessel so that the ground ends of the tubes were covered to a depth of from 2 to 3 cms. Bubbles were removed by gently agitating the bundle of tubes and the gel was allowed to cool and set. On removing the free glass rod the whole of the contents of the jar was easily withdrawn unbroken. Using a keen razor the excess gel was carefully cut away from the ground ends of the tubes and a fine level surface exposed. The filled tubes were then dried and bound in bundles of five to glass rods which projected about 5 cms. beyond the lower ends. These bundles were placed in large cylindrical glass vessels of the gas-jar type, each containing approximately a litre of the normal chloride solution. The projecting 5 cms. of glass rod supported the tubes in about the middle of the solution in the vessels employed. To prevent evaporation from the surface of the diffusing solution and the consequent concentration attendant on this, thick paraffin was poured down the side of the container, so that the surface was covered to a depth of about 0·75 cm. This method was employed in previous determinations by the indicator method, and was shown to prevent completely alterations in concentration due to evaporation (11). Diffusion was allowed to occur upwards into the gels for varying periods, a period of eight days being finally chosen, for reasons given below, the temperature being kept constant in a thermostat in the usual way.

On removal from the solution the tubes were dried singly and treated as follows. Excess solution at the surface of the gel was gently removed by touching with filter paper. Gentle pressure applied to the cork with a glass rod forced the gel in a smooth column from the tube. A definite length forced out was carefully measured, cut off by passing a keen razor across the ground end of the tube and washed into a beaker. Usually four such sections of 1 cm. in length were cut from each tube. The exact height of the centre of each section from the diffusing surface was recorded. About 20 c.c. of distilled water were added to each section and the beakers warmed until a uniform thin gel, which would have a concentration of about 0·1 per cent., was obtained. The concentration of chloride was estimated against 0·1 normal silver nitrate, using 1 c.c. of a 5 per cent. solution of potassium chromate as indicator. The value so obtained for concentration was assumed to be that of the diffusing salt at a point in the gel recorded previously as the height of the centre of the section titrated from the diffusing surface.

In early experiments the calculated coefficients, from data obtained from analysis of the lowest centimetre of the column, showed considerable divergence. The difficulty was to remove excess chloride from the diffusing surface without drawing some of the diffused substance from the gel at the same time. Finally, as no means of avoiding this "end-of-tube error" could be found, the first section analysed was taken so that the distance from the diffusing surface to the centre was 2 cms. This arbitrary choice of the first section analysed made possible the thorough removal of traces of adhering solution from the end of the tube and the surface of the gel, the first 1·5 cms. of which are neglected.

In selecting the time allowed for diffusion another arbitrary choice was made. Preliminary experiments were performed over periods varying from 6 hours to 11 days. It was found that after even two days the concentration of salt at a point 4 cms. from the gel surface was less than 0·1 normal, and consequently the margin of error was too wide to allow of its use in determination of the coefficient. After eight days the concentration of sodium chloride at a point 5 cms. from the free surface of the gel was 0·28 normal at 20°. This rendered possible four calculations of the coefficient of diffusion from each tube. Incidentally this period was also adopted by Öholm (7) in his determinations of coefficients of diffusion in water.

An attempt was made during the course of the investigation to use a gelatin gel as described above for agar-agar, and gels of 5 per cent. and 10 per cent. gelatin were employed. With the 10 per cent. gel it was found necessary gently to warm the tube in order to slide out the gel, and the tendency to adhere to glass exhibited by gelatin made it difficult to cut off accurate lengths. Apart from this difficulty, warming renders the surface of the column of gelatin just liquid and introduces what may be a serious source of error. With a 5 per cent. gel the difficulty of obtaining clean sections was also considerable, and the use of gelatin was abandoned in favour of agar-agar, which in a 2 per cent. gel does not exhibit this strongly adhesive tendency.

Experimental Results.

The factors influencing the rate of diffusion through a 2 per cent. agar-agar gel are: (1) the nature of the diffusing salt; (2) its concentration; and (3) the temperature. The initial concentration of chloride was always normal and determinations of the coefficients of diffusion were made at 20° C. and 30° C.

The results obtained in a single series of experiments where sodium chloride was under investigation are given below.

Table I.—The Coefficient of Diffusion of Sodium Chloride at 20° C. in a 2 per cent. Agar-agar Gel. Initial concentration of the diffusing salt being Normal.

Tube.	Volume per cm. length.	Time in hours.	Concentration of NaCl in Normalities in the cylinder at heights of :—				Coefficients of Diffusion in C.G.S. units × 10^5.				Means.
			2 cm.	3 cm.	4 cm.	5 cm.					
1	0·585 c.c.	192	0·6239	0·4888	0·3418	0·2393	1·203	1·356	1·280	1·310	1·287
2	0·66 c.c.	192	0·6152	0·4682	0·3439	0·2348	1·151	1·237	1·290	1·282	1·240
3	0·595 c.c.	192	0·6268	0·4622	0·3361	0·2370	1·223	1·190	1·251	1·294	1·237
4	0·625 c.c.	192	0·6288	0·4672	0·3312	0·2352	1·238	1·234	1·251	1·285	1·252
5	0·665 c.c.	192	0·6241	0·4737	0·3459	0·2376	1·211	1·268	1·297	1·267	1·261
							1·205	1·257	1·274	1·287	

D (Mean of 20 determinations) = $1 \cdot 256 \times 10^{-5}$.

Table II.—The Coefficient of Diffusion of Calcium Chloride at 30° C. in a 2 per cent. Agar-agar Gel. Initial concentration of the diffusing salt being Normal.

Tube.	Vol. in c.c.s. per cm. length.	Time in hours.	Concentration of Salt in Normalities in the cylinder at—				Coefficients of Diffusion in C.G.S. units × 10^5.				Means.
			2 cm.	3 cm.	4 cm.	5 cm.					
1	0·663	199·7	0·6139	0·457	0·3198	0·2157	1·103	1·126	1·123	1·133	1·121
2	0·651	199·7	0·6252	0·4545	0·3210	0·2217	1·168	1·118	1·131	1·164	1·145
3	0·61	199·7	0·6098	0·4508	0·3164	0·2147	1·07	1·10	1·106	1·127	1·101
4	0·643	199·7	0·5894	0·4370	0·3030	0·2255	1·007	1·034	1·049	1·183	1·068
5	0·452	199·7	0·6084	0·4646	0·3341	0·2234	1·057	1·17	1·190	1·170	1·147
							1·081	1·110	1·120	1·155	

Mean Value of D for 20 determinations = $1 \cdot 116 \times 10^{-5}$.
Calculated P.E. = 0·0077.

The probable error is calculated for the above series (Table I above) on the following expression :—

$$\text{P.E.} = \frac{2}{3}\sqrt{\frac{\Sigma d^2}{n(n-1)}}$$

where $\Sigma\, d^2$ is the sum of squares of differences from the mean and n the number of readings. In the above case the value is 0·007.

Table II gives the results obtained in a similar experiment at 30° where calcium chloride was the diffusing salt.

In Table III are summarised the results obtained for seven chlorides. The numbers representing the concentration of chloride at stated levels are, in the majority of cases, means of five determinations as given in Tables I and II.

In the following table the mean concentrations in columns A are given on the assumption that the concentration of diffusing salt, obtained by analysis of a section of the gel cylinder 1 cm. in length, may be regarded as the actual concentration midway between the cut surfaces.

Comparison of Determinations of Coefficients of Diffusion obtained by Analysis with those obtained by the Indicator Method.

To obtain a fair comparison it is first necessary to apply a correction for gel concentration to either series of results. Determinations were made for diffusion in a 0·5 per cent. gel in the indicator method, while the use of so weak a gel was found to be impracticable in the present method of investigation.

The effect of gel concentration on the rate of diffusion has been investigated by Stiles and Adair (10), who record determinations of coefficients of diffusion of sodium chloride in gels of agar-agar of various concentrations. In the case of sodium chloride the coefficient, calculated for a 0·5 per cent. gel is 1·386, and for a 2 per cent. gel 1·328 at 20·1° C. For the purpose of comparison therefore it is assumed that the coefficients determined in a 2 per cent. gel will be approximately 95·815 per cent. of the coefficients determined in a 0·5 per cent. gel, other factors remaining constant.

In Table IV a summary of the results obtained by both the indicator and chemical analysis methods is given.

Table III.—The Coefficients of Diffusion of Chlorides in a 2 per cent. Agar-agar Gel at 20° C. and 30° C.

Salt.	No. of Exp.	Initial Con. of Salt.	Temp. C.	Time in hours.	A.—Concentration of Chloride in Normalities at heights of—				B.—Coefficients of Diffusion $\times 10^5$ calculated from concentration at				Mean Coeff. in C.G.S. units $\times 10^5$.
					2 cm.	3 cm.	4 cm.	5 cm.	2 cm.	3 cm.	4 cm.	5 cm.	
Sodium chloride	1	N	20°	192	0·6328	0·4720	0·3398	0·2368	1·205	1·257	1·274	1·287	1·256
	2	,,	20°	147·6	0·5918	0·4147	0·2794	0·1753	1·271	1·274	1·286	1·284	1·278
	3	,,	30°	168	0·6417	0·4870	0·3543	0·2535	1·523	1·545	1·540	1·585	1·548
	4	,,	30°	192	0·6660	0·5182	0·3834	0·2770	1·552	1·558	1·538	1·522	1·543
Potassium chloride	1	,,	20°	192	0·6677	0·5361	0·4061	0·3035	1·561	1·702	1·626	1·709	1·662
	2	,,	30°	190·5	—	0·5638	0·4458	0·3486	—	1·979	2·028	2·080	2·029
Lithium chloride	1	,,	20°	197·5	0·6075	0·4460	0·3124	0·2176	1·108	1·099	1·105	1·161	1·118
	2	,,	30°	190	0·6245	0·4752	0·3297	0·2511	1·238	1·292	1·347	1·384	1·315
Ammonium chloride	1	,,	20°	192	0·6729	0·5491	0·4097	0·2954	1·624	1·653	1·699	1·654	1·658
	2	,,	30°	192	0·7043	0·5575	0·4428	0·3470	2·021	1·899	1·960	2·047	1·982
	3	,,	30°	191	0·7014	0·5544	0·4466	0·3447	1·981	1·877	2·010	2·035	1·976
Magnesium chloride	1	,,	20°	191·75	0·5572	0·3858	0·2520	0·1592	0·844	0·870	0·888	0·919	0·878
	2	,,	30°	190	0·5958	0·4297	0·2952	0·2018	1·046	1·065	1·071	1·129	1·078
Calcium chloride	1	,,	20°	190·1	0·5964	0·4165	0·2818	0·1739	1·034	0·996	1·012	0·987	1·008
	2	,,	30°	199·7	0·6093	0·4528	0·3189	0·2202	1·081	1·110	1·120	1·155	1·117
Barium chloride	1	,,	20°	196·4	0·6022	0·4368	0·2936	0·1932	1·022	1·047	1·025	1·048	1·035
	2	,,	30°	197·3	0·6428	0·4837	0·3502	0·2425	1·313	1·293	1·290	1·288	1·296

Table IV.—Comparison of Results of the Indicator and Chemical Analysis Methods for the Determination of Coefficients of Diffusion of Chlorides in a 2 per cent. Agar-agar Gel at 20° C.

Salt.	Initial. Concentration.	Coefficients of Diffusion in C.G.S. units × 10^5.	
		By Indicator method.	By Chemical analysis method.
Ammonium chloride	N	1·610	1·658
Lithium chloride	N	1·219	1·118
Potassium chloride	N	1·619	1·662
Sodium chloride	N	1·328	1·267
Calcium chloride	N	1·145	1·008
Barium chloride	N	1·143	1·035
Magnesium chloride	N	1·107	0·878

Except in the cases of ammonium and potassium chlorides the determinations based on data of penetration are considerably higher than those obtained from data of chemical analysis of successive layers. This somewhat wide divergence was noted in the paper by Stiles and Adair quoted above, who point out that the value of the coefficient of diffusion of sodium chloride in water at 20° C. calculated on Öholm's data derived from an analysis method, is $1 \cdot 31 \times 10^{-5}$ as compared with the value of $1 \cdot 41 \times 10^{-5}$ calculated by extrapolation from their results with gels. This divergence of about 7·5 per cent. could not be accounted for by experimental errors and a suggested explanation was given. "As the free ions diffuse about twice as fast as the undissociated molecules, the coefficient calculated by the indicator method, which measures the rate of penetration of the ions, is bound to be greater than the coefficient calculated on the basis of chemical analysis, in which the total quantity of salt, dissociated and undissociated, is considered." (10.)

The question of diffusion and its connection with the degree of dissociation has been examined in reference to the seven chlorides investigated. According to Arrhenius (2) the degree of dissociation of a salt in solution may be obtained from data of electrical conductivity; thus, percentage dissociation, $\alpha \times 100$

$$= \frac{100 \text{ Molecular conductivity at concentration C}}{\text{Molecular conductivity at infinite dilution}}.$$

Data of equivalent conductivities at 18°, collected from tables by Kohlrausch, Maltby, Grüneisen and Holborn (5), have been employed in the calculation of percentage dissociation ($100\ \alpha$) of the chlorides investigated in normal solution.

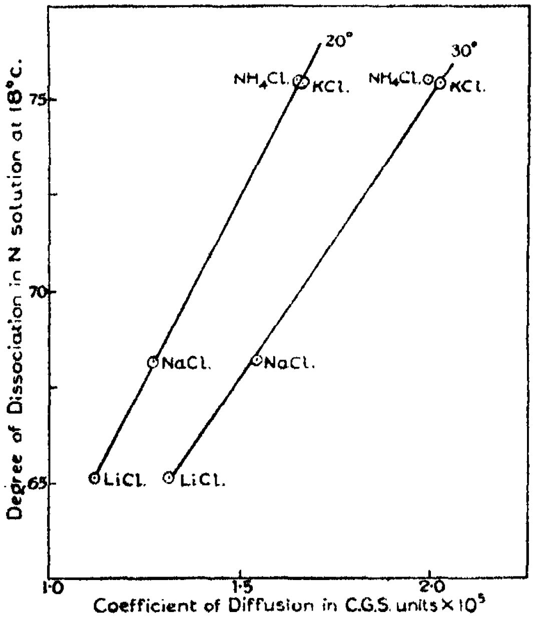
A glance at Table V shows that there appears to be some quite definite relation between the magnitude of the coefficient of diffusion, calculated on data of chemical analysis, and the degree of dissociation of the electrolyte under investigation in solution. Further evidence of this may be obtained on reference to Table III. In columns A and B are given concentrations in normalities and coefficients of diffusion calculated on these data at definite levels in the gel cylinder. Examination of column B shows that there is a marked tendency towards increase in the coefficient of diffusion with decrease in concentration. The mean coefficient given in the last column is such as one would expect from a determination of the concentration of the diffusing salt at a point 3·5 cms. from the surface at which diffusion occurs. This increase in the magnitude of the coefficient of diffusion with decreasing concentration may be accounted for by the fact that with increasing dilution the degree of dissociation of an electrolyte in solution increases. In view of the evidence presented in Table V it appears reasonable to conclude that coefficients of diffusion calculated on data of concentration, where the latter is small, will be considerably higher than determinations at high concentrations. Applied to the indicator method this appears to account for the difference in the results of the indicator and analysis methods. In the indicator method the march of a chloride concentration of approximately 0·00015 per cent. is followed, at which extreme dilution practically the whole of the salt will be dissociated and the calculated coefficient will be correspondingly high.

Table V.—Coefficients of Diffusion of a Number of Chlorides in a 2 per cent. Agar-agar Gel with data of Degree of Dissociation in Normal Solution at 18° C.

Salt.	$D \times 10^5$.		Degree of Dissociation. 100α.
	at 20°	at 30°	
Sodium chloride	1·267	1·548	68·2
Potassium chloride	1·662	2·029	75·5
Lithium chloride	1·118	1·315	65·1
Ammonium chloride	1·658	1·979	75·6 (?)
Magnesium chloride	0·878	1·078	55·1
Calcium chloride	1·008	1·117	58·6
Barium chloride	1·035	1·296	60·0

Furthermore it will be observed that in the case of potassium chloride, where the degree of dissociation is remarkably high, in a normal solution the results obtained by the two methods are more in agreement. The range of degree of dissociation in this case between normal and very dilute solution will not be large and consequently no serious difference in coefficients calculated for different concentrations would be expected. The case of ammonium chloride is similar.

The apparent relation between α, the degree of dissociation, and D, the coefficient of diffusion as obtained in this investigation, is emphasised in the accompanying graph. Moreover the relationship appears to be approximately linear.



The results obtained in this investigation thus indicate that the method of chemical analysis of successive layers, as a means of obtaining the necessary data for the calculation of coefficients of diffusion, yields on the whole lower results than are obtained by the indicator method. The results as exemplified in the case of sodium chloride are similar to those of Öholm, who employed a somewhat similar method in investigating the free diffusion of salts in water. An explanation of this divergence, put forward by Stiles and Adair and quoted earlier in this paper, has received further evidence in its support from results recorded.

Summary.

I. A method for the determination of the coefficients of diffusion of a number of chlorides by means of chemical analysis is described. The method is equally applicable to sulphates and other substances.

II. Coefficients of diffusion of seven chlorides are recorded and compared with the values obtained by the indicator method.

III. An attempt has been made to account for the differences noted in the values obtained by the two methods.

IV. A relationship, apparently linear, between diffusion and the degree of dissociation of the solute is noted.

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An Electrical Method of Determining the Velocity of Detonation of Explosives.

By J. E. P. WAGSTAFF, M.A., Lecturer in Physics, University of Leeds.

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Introduction.

When a layer of molecules in a mass of explosive detonates, the change is transmitted throughout the mass, and the velocity with which the transmission takes place is called the rate of detonation. It has been shown* that the pressure p set up in the front of a detonation wave can be written

$$p = \text{velocity of detonation} \times \text{velocity of vapour} \times \text{density},$$

so that explosives with high rates of detonation will have correspondingly high detonation pressures and consequently high destructive properties. A glance at the accompanying table [*see* Robertson: 'J. C. S.,' vol. 119, p. 1 (1923)], which includes also values for the heat produced during detonation, will show that this is the case :—

Explosive.	Tetryl.	Picric Acid.	Amatol.*	Gun-powder.
Rate of detonation of explosive in m. per sec. (as determined by Dautriche method). Density of loading 1·6 gm. per c.c.	7,500	7,200	5,100	200–300 Density of loading 1·0 gm. per c.c.
Relative pressure produced by explosive in kgm. per cm.^{2} (average peak pressure during $0 \cdot 5 \times 10^{-5}$ sec.). Density of loading 1·3 gm. per c.c.	8,065	7,355	6,001	1,260
Heat produced during detonation of explosive in calories per gm. (water gaseous). Density of loading 1·3 gm. per c.c.	1,090	914	1,004	726

* Ammonium nitrate, 80 per cent.; Trinitrotoluene, 20 per cent.

The pressure developed by tetryl is more than six times that developed by gunpowder, but the number of calories liberated at detonation by 1 gm. is only 1·8 times as great. The detonation pressure therefore depends not only on the amount of energy liberated, but also on the rate at which it is liberated. Rate of detonation becomes therefore at once one of the most important constants in explosive technology.

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* Becker-Bergedorf, 'Zeit. f. Elekchem.,' vol. 23 (1917).

One method at present in use for the absolute determination of the rate of detonation of explosives is that designed by Mettegang and improved by Kast.* The method however possesses disadvantages. In the first place, the velocity of detonation of high explosives (5,000 to 7,000 m. per sec.) is so great compared with the peripheral velocity of a high-speed drum, that, in order to get sparks at a reasonable distance apart, long lengths of material had necessarily to be used.

Apart from the fact that this entailed a considerable amount of work for each round fired, it was only possible to measure the average velocity over a long length of material, and no information could be obtained as to how that velocity varied from point to point. It was with a view to obtaining some direct information on this point that I decided to find the rates of detonation of much shorter lengths. By employing the method to be described, I have been able to obtain with considerable accuracy the velocities for 61 cm. lengths of explosive, and more recently have determined the rate of detonation for a 15·25 cm. length, which involves the measurement of a time interval of 3×10^{-5} second. It has also been possible to use very fine copper wire at the points where the circuits are broken, as the greatest current to be transmitted was only 0·03 amp.

General Principle of the Method.

The method depends on the measurement of the discharge of a condenser during the short interval required for the detonation of a column of explosive. References to previous determinations of short time intervals by the condenser discharge method are given below.† The arrangement which is illustrated in fig. 1 consists of a condenser C in series with a self-inductance L and resistance R. A battery F is sending a small current i amps. round a circuit FUNOH. If the resistance between U and N is R ohms, the potential difference between these two points is Ri volts and a condenser of capacity C farads placed in parallel with this circuit is charged to a potential difference of Ri volts and has a charge RiC coulombs. If the battery be now removed by breaking the circuit at O, this charge of electricity flows round the circuit CLNU and the condenser becomes discharged. Now suppose the circuit FUNOH be passed through a tube of explosive by two wires O and N at a known distance l apart, and suppose moreover that the explosive is detonated and that the detonation wave proceeds in the direction of the arrow with a velocity V cm. per sec. Then immediately the wave reaches O the wire O is broken and the condenser begins to discharge through the circuit CLNU. But for a given value of l by suitably adjusting R, it can be arranged that the condenser only partially discharges during the time interval l/V that it takes the detonation to pass from the position O to N. In these circumstances, when the wire N is broken by the detonation, a part of the charge is left on the condenser. If the quantity of electricity that has disappeared from the plates of the condenser can be measured, the quantity t can be determined from the law governing the rate of discharge, and then from the equation $t = l/\mathrm{V}$, V can be calculated. In this way the absolute determination of a rate of detonation is made to depend and to depend only on a knowledge of the three electrical units, the ohm, the henry, and the farad.

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* Mettegang, 'Report of 5th Cong. Appl. Chem.,' vol. 2, p. 327. Kast, 'Spreng- und Ziendstoffe,' p. 1025.

† Sabine, 'Phil. Mag.,' 1876. Peirce, 'Am. Acad. Proc.,' vol. 13 (1906). Kennelly and Northrup, 'J. Franklin Inst.' (1911).

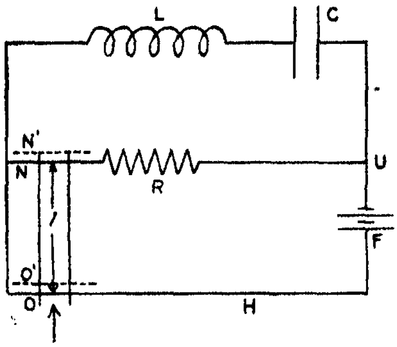

Fig. 1.

Theory of the Method.

Consider a circuit of C farads capacity, R ohms resistance, and L henrys inductance, and suppose that the plates of the condenser are charged to a potential difference of e volts and that the electromotive force is suddenly removed. Measuring t from the instant the electromotive force is removed, if q be the amount of charge left on the condenser t seconds later where $q = q_0 = e\mathrm{C}$, and $dq/dt = 0$, when $t = 0$, the relation between q and t is of the form

$$\frac{d^2q}{dt^2} + \frac{\mathrm{R}}{\mathrm{L}} \cdot \frac{dq}{dt} + \frac{q}{\mathrm{LC}} = 0 \qquad \text{(I)}$$

and the solution of this equation is

$$q = \frac{q_0}{2n}\{(m+n)e^{(-m+n)t} - (m-n)e^{-(m+n)t}\} \qquad \text{(II)}$$

where

$$m = \frac{\mathrm{R}}{2\mathrm{L}} \quad \text{and} \quad n = \sqrt{m^2 - \frac{1}{\mathrm{LC}}}.$$

In the experiment in question t is of the order of 10^{-4} seconds, R is generally about 500 ohms, C is $\frac{1}{4} \times 10^{-6}$ farads, and L, the total unavoidable inductance of the circuit, is 10^{-3} henrys (approximately).

The value of $m = 250 \times 10^3$, and $n = 244 \times 10^3$, so that the negative term in the value for q is negligibly small, and we can write approximately

$$(m - n)\, t = \log_e \left\{ \frac{q_0}{q} \cdot \frac{m + n}{2n} \right\},$$

where the approximate values for the factors are

$$m - n = \frac{1}{\mathrm{RC}}\left(1 + \frac{\mathrm{L}}{\mathrm{R^2C}}\right),$$

and
$$\log_e \frac{m+n}{2n} = \frac{\mathrm{L}}{\mathrm{R^2C}} \left\{ 1 + \frac{5\mathrm{L}}{2\mathrm{R^2C}} \right\};$$

therefore
$$t = \frac{\mathrm{RC}}{1 + \dfrac{\mathrm{L}}{\mathrm{R^2C}}} \log_e \frac{q_0}{q}\left(1 + \frac{\mathrm{L}}{\mathrm{R^2C}}\right),$$

and to the order of accuracy we require, we shall take the law of discharge to be

$$t = \mathrm{RC} \log_e \frac{q_0}{q}. \tag{III}$$

[For the above method of deriving (III) I am greatly indebted to Prof. A. W. Porter, F.R.S.]

Experiments for testing Formula (III).

The first series of experiments undertaken was designed to test this formula and to see how nearly results based on it agree with actual facts for short time intervals of the order of 10^{-4} seconds. It has been shown by Hertz* from mathematical considerations that if two balls of the same material and size, which are free to move in space, strike one another, the time during which they are in actual contact is given by the formula

$$t = 2 \cdot 9432\ \mathrm{R} \sqrt[5]{\frac{25\pi^2 s^2 (1 - \sigma^2)^2}{8 (v - u) \mathrm{E}^2}}, \tag{IV}$$

where R = radius of either sphere in cm.,
s = density of the spheres in gm. per c.c.,
σ = Poisson's ratio for the material,
u and v = the velocities of the balls before impact,
$(v - u)$ being the relative velocity at impact along the line of centres, and
E = Young's modulus for the material in C.G.S. units.

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* Hertz, 'Miscellaneous Papers,' p. 161.

This formula has been completely verified experimentally by Hamburger.* Consider now two suspended steel balls of 2·54 cm. diameter and of density 7·78 gm. per c.c., the one being caused to strike the other with a horizontal velocity of 29·45 cm. per sec., $E = 21 \times 10^{11}$ dynes per cm.^{2} per cm. elongation, and σ is taken $= \frac{1}{4}$, then $t = 0 \cdot 98 \times 10^{-4}$ seconds. This represents the time during which the two balls are actually in contact, and the first point to establish was how nearly this time could be determined by experiments, carried out with the apparatus to be used for the determination of rate of detonation. It might further be noted that for an explosive with a rate of detonation of 7,000 m. per sec., the interval of time required for the detonation of a 61 cm. length is $0 \cdot 87 \times 10^{-4}$ sec. which is of the same order as the time of impact of the two steel balls.

The apparatus is shown diagrammatically in fig. 2. By inserting a plug D, the standard Weston cadmium cell F is made to charge a condenser C of capacity 1/3 m.f. When the condenser is fully charged the plug D is removed. The condenser is subsequently allowed to discharge partially through two suspended steel balls, X and Y, in series with the resistance R, during the time they are in contact.

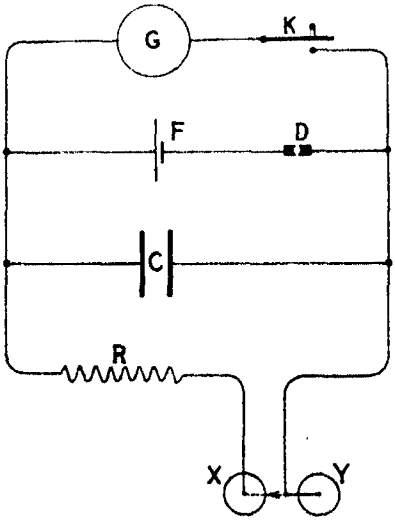

FIG. 2.

The remaining charge on the condenser is now estimated by discharging it through the ballistic galvanometer G by means of the tapping key K, the deflection θ being proportional to q in formula (III). q_0 is similarly estimated by allowing the total charge on the condenser to pass through the galvanometer while the balls are kept apart. If the deflection produced in this case is θ_0,

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* Hamburger, 'Tageblatt d. Nat. Vers. in Wiesbaden' (1887).

$$t = \mathrm{RC} \log_e \frac{q_0}{q}$$

becomes

$$t = \mathrm{RC} \log_e \frac{\theta_0}{\theta}. \tag{V}$$

The swings θ_0 and θ are recorded photographically. Clear photographs of the zero position of the image of the slit and of the position at the end of the first half-swing are formed, and can subsequently be measured to 0·01 cm.

The velocity at impact was obtained from the formula

$$v = \frac{2\pi x}{\mathrm{T}} \tag{VI}$$

where x is the initial displacement, and T is the period of swing of the ball.

In the first series of experiments $x = 8$ cm. and the corresponding velocity of the falling ball at impact was 29·45 cm. per second. Various values of R from 1,000 to 10,000 ohms were used, and the galvanometer throws corresponding to the amount of discharge through these various resistances were photographed. When the throws for different values of R were plotted against R, the points were found to lie on a smooth curve (fig. 3), which approached asymptotically the ordinate corresponding to the total discharge of the condenser. The exponential form of this curve confirmed the assumption that the discharge was

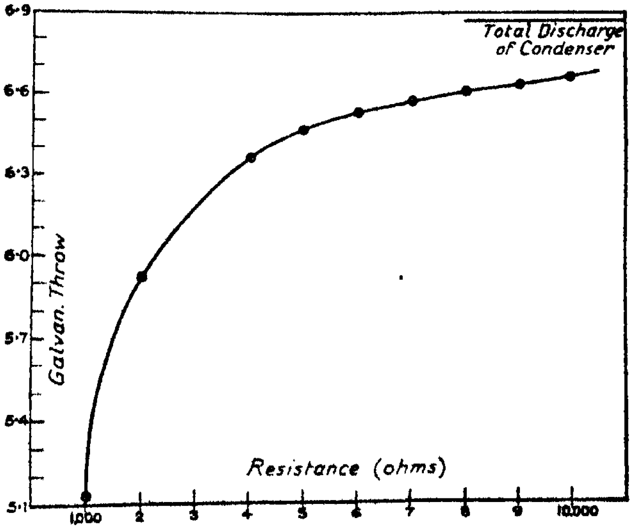

FIG. 3.

viscous for the values of R used. The value of t was then calculated from formula (V), and Table I shows the agreement that could be obtained for varying conditions of discharge. It will be seen that the values of t obtained in different experiments show agreement among themselves and at the same time show a maximum variation of $\pm 0\cdot05 \times 10^{-4}$ sec. from the calculated value.

Table I.

—	Value of R in ohms.	Corresponding galvanometer throws.			Time of impact t in seconds.
Series I	Infinity	6·87	6·87	6·865	—
	10,000	6·66	6·665	6·665	$1\cdot01 \times 10^{-4}$
	5,000	6·485	6·475	6·47	$0\cdot98 \times 10^{-4}$
	4,000	6·37	6·37	6·37	$1\cdot00 \times 10^{-4}$
	2,000	5·93	5·92	5·92	$0\cdot99 \times 10^{-4}$
	1,000		5·14*		$0\cdot97 \times 10^{-4}$
Series II	Infinity	6·84	6·84	6·85	—
	9,000	6·62	6·62	6·635	$0\cdot97 \times 10^{-4}$
	5,000	6·45	6·45	6·45	$0\cdot99 \times 10^{-4}$
	4,000	6·38	6·37	6·35	$0\cdot96 \times 10^{-4}$
	3,000		6·23	6·225	$0\cdot94 \times 10^{-4}$
	2,000	5·91	5·91	5·93	$0\cdot97 \times 10^{-4}$
Series III	Infinity		6·825	6·835	—
	9,000		6·605	6·61	$0\cdot99 \times 10^{-4}$
	5,000	6·46	6·44	6·46	$0\cdot94 \times 10^{-4}$

* Only one observation taken.

Another modification introduced into these experiments was to keep R at a standard value of 5,000 ohms, and vary x so as to have varying velocities of impact.

Table II.—R = 5,000 ohms.

Value of x in cm.	Corresponding galvanometer throw.			Time of impact t in seconds.	$tx^{\frac{1}{5}}$.
8	6·48	6·48	6·475	$0\cdot975 \times 10^{-4}$	$1\cdot48 \times 10^{-4}$
12	6·50	6·50	6·505	$0\cdot914 \times 10^{-4}$	$1\cdot50 \times 10^{-4}$
16	6·52	6·52	6·52	$0\cdot867 \times 10^{-4}$	$1\cdot51 \times 10^{-4}$

Since from formula (IV), for two particular balls, $t = \mathrm{K}/v^{\frac{1}{5}}$ where K is a constant, and since v is proportional to x, $tx^{\frac{1}{5}}$ is constant.

It will be seen from column 4 of the above table that this law is approximately satisfied.

Application of above method to determination of rate of detonation.—Description of Apparatus.

The arrangement is shown diagrammatically in fig. 4. The bomb T, which consisted of a metal tube 0·075 cm. thick and internal diameter 0·43 cm., was fired in a thick steel-lined chamber W, and the effects due to the breaking of the wires O and N were transmitted through three stout, well insulated cables A, B and H to the recording instruments, situated several yards distant in a strongly built chamber, as free as far as possible from mechanical vibration. A series of nine accumulators F was arranged to charge up the condenser through the circuit HOEAK when the plug D was inserted. In order to avoid any disturbing influence in the galvanometer G during this process, the latter was temporarily switched out of circuit by means of the morse key K. A resistance box R was

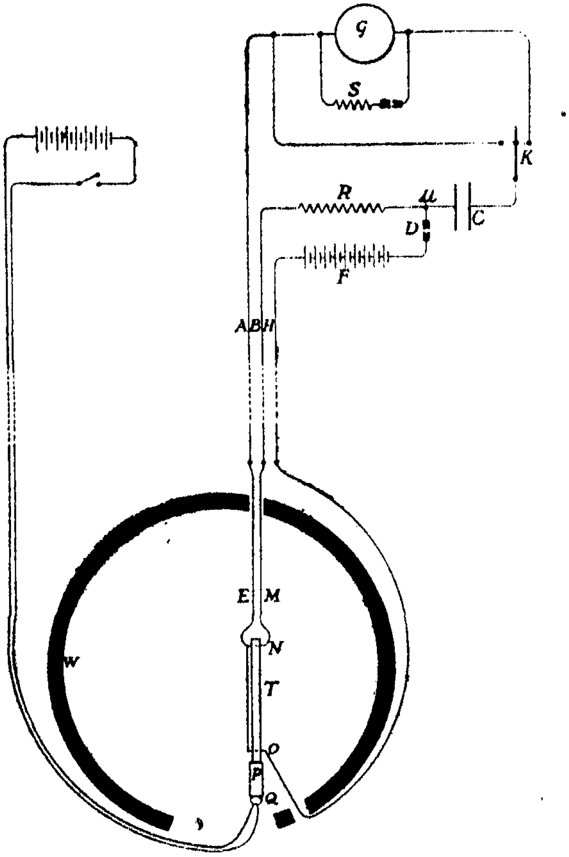

FIG. 4.

placed, as shown, in series with the condenser and the galvanometer, which was rendered dead-beat by shunting it with a resistance S.

The bomb and its connections are shown in detail in fig. 5. The tube containing the explosive was supported about 15 cm. from the floor on a light wooden framework I, and held firmly in position by the two bands Z_1 and Z_2. Fine, well insulated copper wires, N and O (of thickness 0·023 cm.), were passed through the tube of explosive T, containing trinitrotoluene at a density of 1·33 gm. per c.c., at a fixed distance apart, and maintained near their breaking tension by binding them round insulating studs J_1, J_2, J_3, J_4, fixed firmly in the sides of the framework at an angle of about 30° to the vertical. A small quantity of sealing-wax was found to prevent any tendency of the wire to slip and release the tension. The wires E and M, continuous with the cables A and B, and well insulated in rubber tubing, were led into the bomb chamber enclosed in a wooden conduit *a*, while the cable H was similarly continued through a wooden conduit *b* to the wire O. The wooden conduits *a* and *b* were placed in a plane about 15 cm. above that of the bomb to prevent the fine wires E, M, and H, after break, from coming into contact with earth. The battery circuit to one plate of the condenser was completed by joining the two wires N and O by a fine wire from J_1 to J_4 (fig. 5) stretched alongside the bomb. The bomb was initiated by an electric detonator Q, fired from the recording chamber. The metal tube P, which fitted over the end of the bomb, contained the detonator and about 1 gm. of tetryl priming.

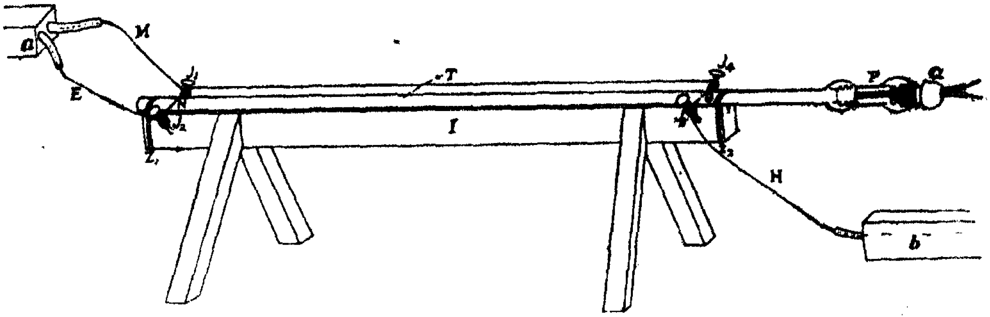

FIG. 5.

Method of using the apparatus for determining a rate.

Assuming that the apparatus is connected up as shown in fig. 4, the condenser is charged as described above. The deflection θ_0 in equation (V) is first obtained by removing the plug D, when the condenser totally discharges through the galvanometer and the shunt. This deflection θ_0 is recorded photographically. To determine the deflection θ corresponding to the quantity of discharge through the galvanometer and shunt while the detonation proceeds from O to N, the condenser is charged up as before and the explosive detonated. The presence of the firing key in the recording chamber enables the galvanometer mirror to be illuminated, immediately preceding the detonation, and thus avoids a long exposure of the plate. The plates are subsequently measured and the rate calculated, as explained in the preceding theory, from the equation

$$t = \mathrm{RC} \log_e \frac{\theta_0}{\theta_0 - \theta}.$$

It can readily be shown that the percentage of the discharge that passed through the galvanometer is independent of the amount of the discharge and of the coefficients of self-inductance of the galvanometer and shunt, and depends only on their relative resistances.

Detailed Account of the Investigation.

(1) Leak in the cables A, B, and H between the chamber W and the recording hut :—In the first few experiments the amount of charge left on the condenser after the detonation was complete was measured. With this method, an interval of half a second or more elapsed after the detonation, before the condenser was discharged through the galvanometer. Experiments were conducted to estimate the amount of the leak of electricity that was likely to occur during this interval, and it was proved that, provided a short length of highly insulating cable was used, the leak during this interval was quite small. It was also found necessary to have the cables as far removed as possible from external circuits (*e.g.*, telegraph wires and power cables), as these caused induced currents in the circuit, to which the galvanometer responded.

(2) Investigation of the amount of discharge through the high temperature flame accompanying the detonation :—This was done by arranging a broken circuit in series with a condenser C and a galvanometer G, as shown in fig. 6 ; the two broken ends were insulated by placing them inside a thin-walled capillary glass tube, as shown in detail in fig. 9 (8). The explosive was detonated and the amount of charge that leaked through the conducting flame between the ends was measured by the galvanometer for different potential differences, over a range comprising those used in the rate of detonation experiments. In a second series, the wires of the broken circuit were passed through the explosive under tension by attaching the free ends to insulated studs on the further side as shown in fig. 9 (10). In this way it was expected to reproduce the conditions

most nearly when a single wire was broken. No material difference between the results of the first and second series was found.

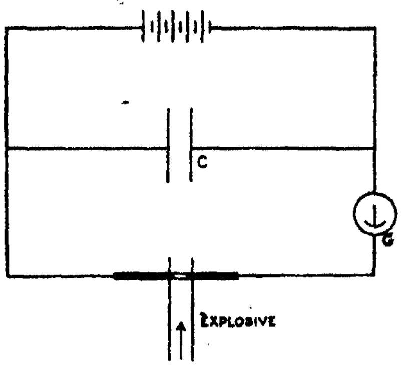

Fig. 6.

In Table III are recorded the throws for different potential differences between the ends of the broken circuit, arranged as in series 2.

Table III.

Potential difference in volts.	Galvanometer throw.	Mean throw.
18	0·74 0·58 0·66 0·56	0·63
12	0·52 0·37 0·40 0·32	0·40
6	0·19 0·18 0·16	0·18

In fig. 7 the mean value of the throw is shown plotted against the potential difference; a linear relation is indicated between these quantities over the

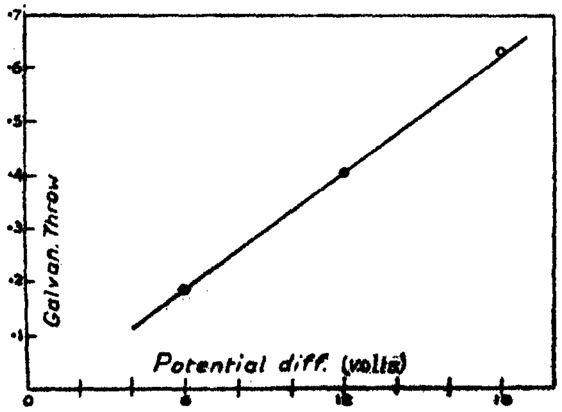

Fig. 7.

range tested. It is important to notice that the gas effect occurs both at O and N (fig. 1) and in both cases delays the instantaneous break of the circuit. At O this has the effect of keeping the condenser charged to its full potential difference for an extra time, δt, during which the detonation has proceeded to O′. At N it has the effect of allowing the condenser to discharge for an extra time, δt_1, during which the detonation has proceeded to N′. It is in fact the time interval between O′ and N′ that is measured.

Now the amount of discharge through the flame during a time interval δt can be written

$$q = i\,\delta t = \mathrm{CNUX}\,\delta t,$$

where N = number of ions per unit volume in the gases,
U = mobility of ions at the temperature of the flame,
X = electrostatic field,
C = a constant which involves the amount of the ionic charge.

Fig. 7 indicates that q/X is constant over the range used, so that δt is independent of X or the delays at O and N are independent of the electrostatic conditions at these points, and any differences between δt and δt_1 are due to differences in delay in the actual breaking of the wires and thus can be reduced considerably by using extremely fine wire stretched almost to breaking tension.

(3) Preliminary experiments on rate of detonation.

In the first few trials, the battery F consisted of one accumulator only and the explosive was fired with a No. 5 Nobel detonator and Bickford fuse. Owing to the photographic device used for recording the swing, this method of firing proved unsatisfactory. An attempt to use instantaneous fuse was soon abandoned in favour of the electric detonator which was fired from the recording chamber. In these preliminary experiments also the time interval was calculated from measurements of the amount of charge remaining on the condenser, but this was soon abandoned, owing to the uncertainty of the leak in the interval between the detonation and the subsequent discharge of the condenser through the galvanometer circuit, in favour of the modification, whereby the discharge itself passed through the galvanometer. The results then obtained were erratic and the investigation of this variation was next undertaken.

(4) The investigation and elimination of the E.M.F. set up in the circuit at break.

An experiment was arranged in which a copper wire from the plates of the condenser in series with the galvanometer passed through the explosive as shown in fig. 8. When the explosive was detonated, a quantity of charge passed round the circuit in the direction indicated. Various modifications of the experiment were tried with the wire passing over or under the explosive as shown in fig. 9 (2 and 3). In every case a charge passed round the circuit in the same direction without exception, and the effect was larger for wires passing through than for wires passing under or over.

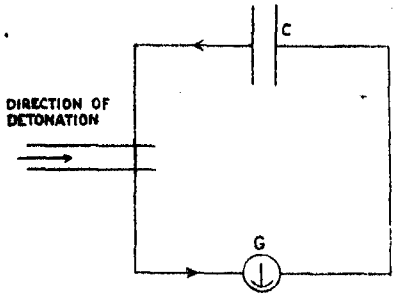

Fig. 8.

Attempts were made to eliminate the effect by arranging systems of wiring as shown in fig. 9 (4, 5, 6, and 7), but although in some instances partial compensation seems to have been effected, the method of dealing with the difficulty was quite unsuccessful. It was found that when a broken wire passed through the explosive no such effect was observed, so that the phenomenon occurred before the wire was broken. Any influence due to the initiation of the explosive with an electric detonator was shown to be absent by arranging trials in which the explosive was fired with trade detonators (not electric) and electric detonators respectively. The effect in the two cases was of precisely the same order.

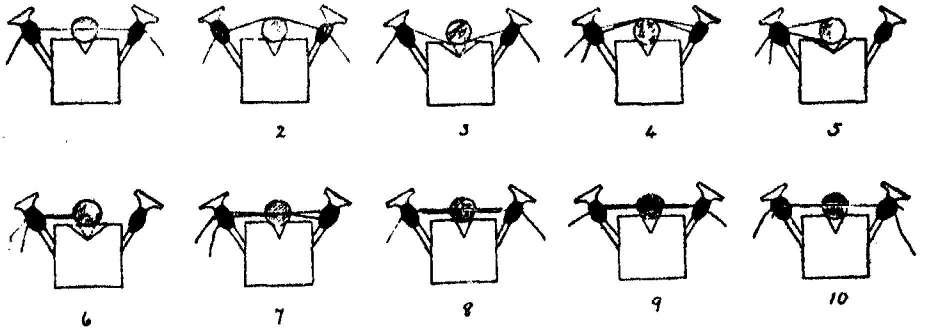

Fig. 9.

The phenomenon was finally shown to be associated with the Thomson thermo-electric effect, by experiments in which the copper wire through the explosive was replaced by iron and lead wires respectively. With the iron wire a throw of the galvanometer was observed in the direction opposite from that with copper, while in the case of the lead wire the effect was scarcely observable. While the use of lead wire would have reduced very considerably the importance of the effect, it is a very unsatisfactory material to handle, especially under tension, and it was found more convenient to overwhelm the effect by increasing the number of accumulators from one to nine, at the same time shunting the galvanometer. Increasing the E.M.F. to 18 volts made the effect of comparatively very small importance, and at the same time the marked damping of the galvanometer caused by the shunt (which rendered it dead-beat) completely eliminated it. A shunt of 100 ohms with 18 volts in circuit, while producing a sufficiently marked damping effect to eliminate completely the transient E.M.F. at the same time gave a deflection of the galvanometer of the same order as that previously obtained with 2 volts and no shunt.

(5) As the results now obtained were much more consistent, several determinations were made of the rate of detonation of trinitrotoluene at a density of 1·33 gm. per c.c., enclosed in a lead tube of 0·43 cm. bore and 0·075 cm. thickness. The distance l was made 61 cm. long and the cross wires at O and N were 0·023 cm. in diameter, and maintained almost at their breaking tension. A table of results is appended.

Table IV.—Resistance of Galvanometer = 100 ohms.

Resistance of shunt (ohms).	Total resistance in circuit (ohms).	θ_0.	$\theta_0 - \theta$.	Rate of detonation (m. per sec.).
100	550	6·57	3·37	4,980
100	550	6·57	3·50	5,280
100	550	6·94	3·61	5,090
100	550	7·03	3·56	4,880
100	550	6·80	3·50	5,000
100	550	6·78	3·44	4,900
100	550	6·78	3·45	4,920
100	550	6·77	3·53	5,110
100	550	6·77	3·51	5,060
100	550	6·90	3·37	4,640
100	550	6·745	3·515	5,100
100	550	6·745	3·525	5,120
100	550	6·80	3·35	4,700

The mean rate of detonation for the 13 experiments is 4,990 m. per sec. The tube has been tested by the Mettegang apparatus and found to have a rate of detonation of 5,000 m. per sec.

This series on 61 cm. lengths was now repeated, but using cross wires only 0·008 cm. thick. The results of the five rounds fired under these conditions are given in the following table :—

Table V.

Resistance of shunt (ohms).	Total resistance in circuit (ohms).	θ_0.	$\theta_0 - \theta$.	Rate of detonation (m. per sec.).
100	550	6·54	3·38	5,040
100	550	6·54	3·33	4,920
100	550	6·54	3·29	4,840
100	550	6·54	3·38	5,040
100	550	6·54	3·31	4,880

Several rounds were now fired for a value of $l = 30 \cdot 5$ cm. and in which the cross wires were 0·023 cm. in diameter. It will be noticed that the results are much more variable than those given in the preceding table.

Table VI.

Resistance of shunt (ohms).	Total resistance in circuit (ohms).	θ_0.	$\theta_0 - \theta$.	Rate of detonation (m. per sec.).
60	237·5	4·21	1·94	4,970
60	237·5	4·21	1·83	4,620
100	550	6·92	4·76	4,450

But immediately the cross wires were reduced from 0·023 cm. to 0·008 cm. in diameter, the results acquired greater uniformity. As we are here measuring a time interval of 6×10^{-5} sec. any delay in the breaking of the wires becomes of much greater importance, and therefore the greater variability with the thicker wire is to be expected.

Table VII.

Resistance of shunt (ohms).	Total resistance in circuit (ohms).	θ_0.	$\theta_0 - \theta$.	Rate of detonation (m. per sec.).
100	250	6·53	3·12	4,955
100	250	6·53	3·04	4,780
100	250	6·53	3·14	4,990
100	250	6·53	3·26	5,280
100	250	6·50	3·12	4,980
100	250	6·50	3·12	4,980

This gives a mean rate of detonation of 4,980 m. per sec.

Still one more series was fired in which $l = 15 \cdot 25$ cm. and the cross wires 0·008 cm. diameter.

Table VIII.

Resistance of shunt (ohms).	Total resistance in circuit (ohms).	θ_0.	$\theta_0 - \theta$.	Rate of detonation (m. per sec.).
100	250	6·91	4·73	4,830
100	150	6·82	3·44	4,450
100	150	6·71	3·71	5,145
100	150	6·60	3·43	4,600
100	150	6·60	3·40	4,600
100	150	6·59	3·52	4,860
100	150	6·40	3·45	4,930
100	150	6·40	3·52	5,100
100	150	6·40	3·33	4,670

This gives a mean rate of detonation over a 15·25 cm. length of explosive of 4,810 m. per sec.

(6) As a further modification the rates of detonation of three other widely different explosives were determined by this method, and the results compared with those previously obtained by other investigators.

Table IX.—l = 30·5 cm., cross wires 0·008 cm. diameter.

Explosive.	Number of rounds fired.	Mean rate of detonation or explosion (m. per sec.).	Rate of detonation quoted by other investigators.
Tetryl, density 1·45 gm. per c.c. fired in a steel tube of 0·6 cm. bore and walls 0·06 cm. thick.	4	7,530	7,520 based on results by Mettegang apparatus.
Fulminate of mercury loose in a brass tube of 0·6 cm. bore and 0·16 cm. walls.	2	3,370	2,250 (Kling and Florentin), 3920 (Bichel).
Mealed powder	1	265	200–300 (Bichel).

The method of determining rates of detonation described above has so far been used to a small extent only. The results are by no means as regular as were expected from the theoretical considerations. The divergence is undoubtedly to some extent inherent in the method, but it is also partly due to variations in the actual rate of detonation of the explosives tested. As a means of determining the rate of detonation of explosives, available in small quantities only, the method should be of value.

The experiments described in this paper were performed at the Research

Department, Royal Arsenal, Woolwich, during 1918 and the early part of 1919. In January, 1920, a paper by Klopsteg appeared in the 'Physical Review,' vol. 15, describing experiments for the determination of the velocity of projectiles by a somewhat similar method, and in July, 1921, a short note was published in 'Nature' by Pollard, on the measurement of single and successive time intervals.

Summary.

(1) A method, depending on the rate of discharge of a condenser, is developed for the measurement of time intervals of the order of 10^{-4} sec.

(2) The method is tested by finding the time of impact of steel balls.

(3) The method is applied to the measurements of rates of detonation of high explosives.

(4) Spurious electrical effects, occurring in a circuit passing through the explosive, are investigated and methods of elimination discussed.

My thanks are due to my friend Mr. W. B. Foden, B.A., for his valuable assistance during the progress of the work; to Dr. Godfrey Rotter for kindly revising the manuscript; to Sir Robert Robertson for his kindly interest and encouragement; and to the Director of Artillery for granting permission to publish the paper.

The Series Spectrum of Ionised Carbon (C II).

By A. Fowler, F.R.S., Yarrow Research Professor of the Royal Society,
Imperial College, South Kensington.

(Received February 15, 1924.)

Introductory.

For the development of the theory of atomic structure there would appear to be a special need for data relating to the series spectra of the lighter elements. It has, therefore, been thought desirable to publish the present account of the series of singly-ionised carbon without waiting for the completion of the investigation of the spectrum at other stages of ionisation.

It is an essential feature of Bohr's quantum theory of spectra that while the series constant for neutral atoms is nearly the same as that for hydrogen, the value of this constant will be increased four times when the atom is singly ionised, nine times when it is doubly ionised, 16 times when it is trebly ionised, and so on. Evidence that a system of series represents a particular stage of ionisation is thus to be sought in the value of the series constant for the system in question. Experimental confirmation has been obtained as far as the second ionisation by Paschen in the case of aluminium,* and as far as the third ionisation by the present writer in the case of silicon.†

The system of series dealt with in the present paper is characterised by a fourfold value of the hydrogen constant, and is accordingly attributed to singly-ionised carbon. The series may thus be designated C^+ or C II, those of the neutral atom being indicated by C or C I.

It may be remarked that the series of C I have not yet been identified. The only line which occurs in the arc spectrum in the ordinary region of observation is the well known line λ 2478, and observations in the extreme ultra-violet have hitherto only been made under conditions which generate the spectra of ionised atoms in addition to those of neutral atoms. The elimination of lines due to ionised atoms may perhaps simplify the identification of those belonging to the neutral atoms.

Experimental Procedure.

Extensive observations of the spectrum of carbon have been made over a wide range of wave lengths and under a variety of experimental conditions. The sources included the spark between graphite poles in air, the spark in hydrogen, the arc *in vacuo*, and carbon compounds—chiefly carbon-dioxide and hydrocarbons—in vacuum tubes. In connection with the vacuum tube observations the spectrum of oxygen under similar varied conditions was also investigated, so that the carbon lines could be distinguished in the mixed spectra of carbon and oxygen. The vacuum-tube spectra yielded lines of fine definition, which could be accurately measured in most cases. In the spark spectrum, the carbon lines are mostly diffuse, especially in the ultra-violet.

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* 'Ann. d. Phys.,' vol. 71, p. 142 (1923).

† 'Roy. Soc. Proc.,' A, vol. 103, p. 413 (1923).

Several of the lines in the ordinary region of observation which enter into the present discussion have been previously recorded, but few of them had been measured with sufficient accuracy for the present purpose. Among the newly-observed lines are a pair in the extreme red and three pairs in the ultra-violet.

Several spectrographs were utilised in the investigation, including a 10-foot concave grating, two large glass spectrographs, a quartz-Littrow spectrograph (Hilger's E 1), and a quartz spectrograph of ordinary construction (Hilger's E 2).

The standard lines adopted were those of iron, except in the region λ 2200 to λ 2100, for which Eder's wave-lengths of the copper spark lines* were used.

Several photographs have also been taken with a vacuum grating spectrograph. The carbon lines in the extreme ultra-violet, however, have already been measured by Simeon,† Millikan,‡ Hutchinson,§ and others. The wave-lengths and intensities given by these observers for lines which are believed to originate in C II are indicated in Table I.

The source employed by Simeon was the carbon arc in vacuo, while Millikan observed the spectrum of the "vacuum spark," and both sources were used by Hutchinson. There is a fairly close agreement between Simeon and Millikan, except for the last line, but the method of coincidences followed by Simeon is probably the most trustworthy, and Simeon's wave-lengths have accordingly been adopted. Evidence of their general accuracy is afforded by the close agreement of these wave-lengths with those calculated from the well-determined lines in the ordinary region of observation, as will appear from Table III. It may be noted that the pair of lines λ 1036 appeared in the second order on a plate of the carbon arc *in vacuo* taken in the course of the present investigation, and was very clearly resolved ; the less refrangible component was decidedly the brighter, as would be expected from the series discussion, though both were assigned intensity 5 by Simeon.

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* 'Zeit. f. Wiss. Phot.,' vol. 13, p. 24 (1914).

† 'Roy. Soc. Proc.,' A, vol. 102, p. 484 (1922), and vol. 104, p. 368 (1923).

‡ 'Astrophys. Jour.,' vol. 53, p. 159 (1921).

§ 'Astrophys. Jour.,' vol. 58, p. 291 (1923).

Table I.—Wave-lengths of C II Lines in Extreme Ultra-violet.

Simeon.		Millikan.		Hutchinson.		
	Intensity.		Intensity.		Intensity.	
					Arc.	Spark.
1036·84	5	1036·7	12	1037·2	10	8
1036·22	5					
858·2	7	858·5	5	858·9	8	7
687·1	7	687·3	8	687·1	6	8
636·2	2	636·3	3	636·8	—	2
594·9	4	595·1	5	595·5	1	5
560·5	2	560·5	2	562·0	—	1
543·4	1	543·5	1	544·0	—	0
533·9	1	533·3	1	—	—	—

Notation and Numeration.

The series rotation adopted is mainly that of the author's "Report on Series in Line Spectra."* Following the recent papers of Bohr and Paschen, however, the designation of the terms of the diffuse series has been changed, so that the terms $m\delta$, $m\delta'$ have become $m\delta_1$ and $m\delta_2$ respectively. This has the advantage of bringing the nomenclature of the diffuse terms into accordance with that for the terms of the principal series, lines involving π_1 or δ_1 being of greater intensity than those involving π_2 or δ_2. The use of Greek letters is merely to indicate that a system of doublets is under consideration.

The Rydberg and Ritz systems of numeration of the spectral terms have also been radically changed by Bohr on theoretical grounds, and in view of their possible permanence the new numbers have been introduced into the tables which follow. The numbers on the Rydberg system, however, are also given (in brackets) to facilitate comparison with earlier tables of series. It may be remarked that the empirical formulæ of Rydberg, Ritz and Hicks give no direct indication of Bohr's numbers, although they can be adapted to include them. On the new system, groups of electrons in the normal atom, such as were formerly supposed to be arranged in rings about the nucleus, are characterised by successive principal quantum numbers increasing outwards, and the four outer electrons in the carbon atom (atomic No. = 6) are accordingly assigned the quantum number 2. The subsidiary, or azimuthal, quantum number, however, is not necessarily or usually the same for all the electrons of a group.

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* Physical Society, London, p. 18 (1922).

Identification of the Series.

From the beginning of the investigation it seemed probable that the well-known pair of spark lines in the red, near λ 6580, must belong to a principal series. Existing data* suggested that pairs of lines about λ 2837 and λ 3920 might have the same separation and be associated with the red pair. The experimental work confirmed this equality of separation and revealed similarly related pairs about λ 2747 and λ 2402. With these data, omitting the pair at λ 2837 and assuming the series constant to be 4N, the main features of the series were suggested, and the approximate positions of other lines were calculated. Special search for these lines was instituted, and some of them were identified, notably a pair in the extreme red about λ 7236 and a second member of the principal series at λ 2174. The identification of this red pair led in turn to the recognition of the fundamental series, the first member of which is the well-known spark line at λ 4267. Much embarrassment was caused throughout by the strong pair at λ 2837, which apparently had no place in the series thus suggested.

It was clear that associated stronger series might be expected in the extreme ultra-violet. An approximate limit for the subordinate series, 2 (1) π, could be calculated from the two π terms already obtained, and thence the approximate positions of lines by the use of the already known terms. The identifications, however, were actually made by sorting out wave-numbers which differed by the same amounts as the known terms, assuming that the tabulated lines were unresolved doublets. Next, with a Hicks formula, the three lines λλ 594·9, 560·5 and 543·4, with 4N for series constant, led to the limit 2 (1) π_1 = 196643, but this might have been considerably in error because of the great influence of small errors of wave-length on the wave-numbers. A more exact value of the limit was obtained through the outstanding pair at λ 2837 and the strong pair at λ 1036 by introducing a term x as shown under "combinations" at the foot of Table III. In this way, the separation ($\Delta\nu = 58$) of the pairs of the series in the extreme ultra-violet was deduced.

The significance of the x term is not clear. It is probable, however, that it is of the σ type, because it gives the normal separation to the pair at λ 2837 and

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* Kayser's 'Handbuch,' vol. 5, p. 225.

Table II.—List of C II Lines.

λ, I.A.	Intensity.	ν.	Series.	Remarks.
† 7236·19	8*n*	13815·63	$3(2)\pi_1-3(2)\delta_1$	Grating, 5·5 A per mm.
7231·12	6*n*	13825·31	$3(2)\pi_2-3(2)\delta_2$	
6582·85	8	15186·80	$3(2)\sigma-3(2)\pi_2$	Grating, 5·5 A per mm.
6578·03	10	15197·93	$3(2)\sigma-3(2)\pi_1$	
5891·65	2	16968·48	$4(3)\pi_2-4(2)\delta_2$	Glass sp., 10 A per mm.
5889·97	3	16973·32	$4(3)\pi_1-4(2)\delta_1$	
‡ 4267·27	10*n*	23427·61	$3(2)\delta_1-4(3)\phi$	Glass sp., 2·6 A per mm.
4267·02	8*n*	23428·99	$3(2)\delta_2-4(3)\phi$	
3920·773	8	25497·98	$3(2)\pi_1-4(3)\sigma$	Glass sp., No. 2, 4·6 A per mm.
3919·061	6	25509·11	$3(2)\pi_2-4(3)\sigma$	
2992·63	4*n*	33405·71	$3(2)\ \delta-5(4)\phi$	Quartz sp. E 1, 4·6 A per mm.
2837·602	8	35230·69	$x\ -3(2)\pi_2$	Grating, 2·8 A per mm.
2836·710	10	35241·75	$x\ -3(2)\pi_1$	
¶ 2747·31	6*n*	36388·52	$3(2)\pi_1-4(3)\delta_1\delta_2$	Quartz spec. E 1, 3·7 A per mm.
2746·50	4*n*	36399·24	$3(2)\pi_2-4(3)\delta_2$	
§ 2574·86	1*n*	38825·45	$3(2)\delta-6(5)\phi$	Quartz spec. E 1, 3·1 A per mm.
* 2402·40	2*n*	41612·37	$3(2)\pi_1-5(4)\sigma$	Quartz spec. E 1, 2·4 A per mm.
2401·77	1*n*	41623·27	$3(2)\pi_2-5(4)\sigma$	
† 2174·14	1	45980·82	$3(2)\sigma-4(3)\pi_2$	Quartz spec. E 2, 5·5 A per mm.
2173·86	2	45986·74	$3(2)\sigma-4(3)\pi_1$	
† 2137·93	1*n*	46759·34	$3(2)\pi_1-5(4)\delta_1\delta_2$	Quartz spec., E 2, 5·3 A per mm.
2137·45	1*n*	46769·84	$3(2)\pi_2-5(4)\delta_2$	
‖ 1036·84	5	96447	$2(1)\pi_1-x$	Vacuum sp. (Simeon).
1036·22	5	96505	$2(1)\pi_2-x$	
858·2	7	116523	$2(1)\pi-3(2)\sigma$	Vacuum sp. (Simeon). Unresolved pair.
687·1	7	145539	$2(1)\pi-3(2)\delta$	Vacuum sp. (Simeon). Unresolved pair.
636·2	2	157183	$2(1)\pi-4(3)\sigma$	Vacuum sp. (Simeon). Unresolved pair.
594·9	4	168095	$2(1)\pi-5(4)\delta$	Vacuum sp. (Simeon). Unresolved pair.
560·5	2	178412	$2(1)\pi-5(4)\delta$	Vacuum sp. (Simeon). Unresolved pair.
543·4	1	184026	$2(1)\pi-6(5)\delta$	Vacuum sp. (Simeon). Unresolved pair.
533·9	1	187301	$2(1)\pi-7(6)\delta$	Vacuum sp. (Simeon). Unresolved pair.

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* Eder & Valenta, 2402·1 (1*n*).

† Not previously recorded.

‡ First resolved by A. S. King ('Astrophys. Jour.,' vol. 38, p. 329 (1913).

§ Eder & Valenta, 2576·7 (1).

‖ The less refrangible line is the stronger.

¶ Eder & Valenta, 2747·3 (3).

leads to no fundamental series if supposed to be of δ type. There is a somewhat similar term in the series of Si II, as will be shown in a subsequent paper, but in that case it is certainly of δ type.

The lines which are considered to be definitely included in the series system of ionised carbon are brought together in the order of wave-lengths in Table II, which is self-explanatory. Wave-lengths from 1036 A downwards are the values *in vacuo* according to the measurements of Simeon. Particulars as to the instruments used for the determination of individual wave-lengths are given in the last column of the table, which also indicates the dispersion in Angstroms per millimetre at the respective wave-lengths. On account of the diffuse character of some of the lines, the accuracy of the wave-lengths is probably not in every case commensurate with the dispersion employed, but the errors are not likely to exceed a few hundredths of an Angstrom.

Several lines which occur in the carbon spark are not included in the above list and may possibly belong to series representing higher degrees of ionisation. Many lines which do not appear in the spark have, in fact, been obtained by passing strong discharges through carbon compounds in vacuum tubes.

The Series Limits.

Justification for the adoption of 4N as the series constant for the spectrum under consideration is found in the consistency of the various terms when this assumption is made in the calculation of limits. With the exception of the first diffuse series, there is unfortunately no observed series which is long enough to permit the use of a four-constant formula. This series is not very suitable for the independent calculation of the series constant, partly because diffuse series are often imperfectly represented by formulæ, and partly because of the possible large errors in the wave-numbers, but the following formula may be quoted as representing the first four members :—

$$\nu = 197003 - 487868 \bigg/ \left(m + 1\cdot166484 - \frac{0\cdot175114}{m}\right)^2.$$

The value of the constant thus calculated is 4·45N, which is, perhaps, as near to 4N as is to be expected from the nature of the data. As indicating the uncertainty in the calculation of the constant from this series it may be noted that a decrease of only one-tenth of an Angstrom in the wave-length of the line λ 560·5 leads to the value 436018 or 3·975N, and the limit 196500.

More exact values of the limits and spectral terms may be derived from the measurements in the ordinary region of the spectrum, for which greater dispersion could be utilised. Formulæ were accordingly calculated as follows :—

2nd Sharp Series. $3(2)\pi_1 - m\sigma$.

$$\begin{array}{r} -15197\cdot93 \\ 25497\cdot98 \\ 41612\cdot37 \end{array} \left\{ \begin{array}{l} \nu = 65045\cdot37 + 4N \Big/ \left(m + 0\cdot315569 + \dfrac{0\cdot045305}{m}\right)^2 \\ 3\,(2)\,\pi_1 = 65045\cdot37 \\ 3\,(2)\,\pi_2 = 65056\cdot50 \end{array} \right.$$

2nd Diffuse Series. $3\,(2)\,\pi_2 - m\delta_2$.

$$\begin{array}{r} 13825\cdot31 \\ 36399\cdot24 \\ 46769\cdot84 \end{array} \left\{ \begin{array}{l} \nu = 64888\cdot50 + 4N \Big/ \left(m + 0\cdot910270 + \dfrac{0\cdot041740}{m}\right)^2 \\ 3\,(2)\,\pi_1 = 64877\cdot37 \\ 3\,(2)\,\pi_2 = 64888\cdot50 \end{array} \right.$$

Fundamental Series. $3\,(2)\,\delta_1 - m\phi$.

$$\begin{array}{r} 23427\cdot61 \\ 33405\cdot71 \\ 38825\cdot45 \end{array} \left\{ \begin{array}{l} \nu = 51107\cdot56 + 4N \Big/ \left(m + 0\cdot969722 + \dfrac{0\cdot034111}{m}\right)^2 \\ 3\,(2)\,\pi_1 - 3\,(2)\,\delta_1 = 13815\cdot63 \\ 3\,(2)\,\pi_1 = 64923\cdot19 \\ 3\,(2)\,\pi_2 = 64934\cdot32 \end{array} \right.$$

The mean of the three values for $3(2)\pi_1$ is 64948, but since the negative wave-number in the 2nd sharp series is unfavourable to a good determination of the limit, and diffuse series are usually not well represented by the empirical formulæ, it has been considered best to adopt the values determined from the fundamental series, namely,

$$3\,(2)\,\pi_1 = 64923\cdot19$$
$$3\,(2)\,\pi_2 = 64934\cdot32$$

The limits of the other series then follow when the corresponding terms and lines are combined in the usual manner. The decimal parts have, of course, no claim to significance, and are only retained to preserve accuracy in the combination of terms.

The Series System of C II.

Details as to the various series of C II which have so far been traced are given in Table III, which is arranged on the plan adopted in the author's "Report on Series," and calls for little further explanation. It is only necessary to note that the lines of the first sharp and first diffuse series have not been resolved, and that their separations have been assumed to be the same as the separation of the pair at λ 1036, as measured by Simeon. Assuming the latter to have been accurately measured, the positions of the other members in the region of short

Table III.—Series of C II.

1st Sharp Series. $2(1)\pi - m\sigma$.
$2(1)\pi_1 = 196612$; $2(1)\pi_2 = 196670$.

Observed.		Calculated.		Δν.	m	mσ.
λ, Intensity.	ν.	λ.	ν.			
					B. R.	
858·2 (7)	116523	858·43 858·00	116491 116549	[58]	3 (2)	80121
636·2 (2)	175183	636·18 635·95	157187 157245	,,	4 (3)	39425
—	—	577·03 576·83	173301 173359	,,	5 (4)	23311
—	—	551·80 551·63	181225 181283	,,	6 (5)	[15387]

1st Diffuse Series. $2(1)\pi - m\delta$.
$2(1)\pi_1 = 196612$; $2(1)\pi_2 = 196670$.

Observed.		Calculated.		Δν.	m.	mδ.
λ, Intensity.	ν.	λ.	ν.			
					B. R.	
687·1 (7)	145539	687·27 686·99	145504 145562	[58]	3 (2)	51108
594·9 (4)	168095	594·96 594·76	168077 168135	,,	4 (3)	28585
560·5 (2)	178412	560·39 560·21	178448 178506	,,	5 (4)	18164
543·4 (1)	184026	543·32 543·15	184054 184112	,,	6 (5)	[12558]
533·9 (1)	187301	533·56 533·40	187419 187477	,,	7 (6)	[9193]

Fundamental Series. $3(2)\delta - m\phi$.
$3(2)\delta_1 = 51107{\cdot}56$; $3(2)\delta_2 = 51108{\cdot}94$.

λ, Intensity.	ν.	Δν.	m	mφ.	Remarks.
			B. R.		
4267·27 (10) 4267·02 (8)	23427·61 23428·99	1·38	4 (3)	27679·95	
2992·63 (4*n*)	33405·71	—	5 (4)	17702·54	Mean $\delta_1\delta_2$ taken.
2574·86 (1*n*)	38825·45	—	6 (5)	12282·80	Mean $\delta_1\delta_2$ taken.
[2375·1]	[42091]	—	—	[9017·0]	

Table III—*continued*.

Principal Series. $3(2)\sigma - m\pi$.
$3(2)\sigma = 80121\cdot12$.

λ, Intensity.	ν.	Δν.	*m*.	$m\pi_1$, $m\pi_2$.
			B. R.	
6578·03 (10) 6582·85 (8)	15197·93 15186·80	11·13	3 (2)	64923·19 64934·32
2173·86 (2) 2174·14 (1)	45986·74 45980·82	5·92	4 (3)	34134·38 34140·30

2nd Sharp Series. $3(2)\pi - m\sigma$.
$3(2)\pi_1 = 64923\cdot19$; $3(2)\pi_2 = 64934\cdot32$.

λ, Intensity.	ν.	Δν.	*m*.	$m\sigma$.
			B. R.	
−6578·03 (10) −6582·85 (8)	−15197·93 −15186·80	11·13	3 (2)	80121·12
3920·773 (8) 3919·061 (6)	25497·98 25509·11	11·13	4 (3)	39425·21
2402·40 (2*n*) 2401·77 (1*n*)	41612·37 41623·27	10·90	5 (4)	23310·82
[2018·1] [2017·6]	[49536] [49547]		6 (5)	[15387]

2nd Diffuse Series. $3(2)\pi - m\delta$.
$3(2)\pi_1 = 64923\cdot19$; $3(2)\pi_2 = 64934\cdot32$.

λ, Intensity.	ν.	Δν.	*m*.	$m\delta_2$, $m\delta_1$. ($m\delta'$, $m\delta$.)
			B. R.	
§ — 7236·19 (8*n*) 7231·12 (6*n*)	[13814·18] 13815·63 13825·31	[1·45] [11·13]	3 (2)	51109·01 51107·56
§ — 2747·31 (6*r*) 2746·50 (5*r*)	[36388·11] 36388·52 36399·24	[0·41] [11·13]	4 (3)	28535·08 28534·67
2137·93 (1*n*) 2137·45 (1*n*)	46759·34 46769·84		5 (4)	18164·2
			6 (5)	[12558]
			7 (6)	[9193]

3rd Diffuse Series. $4(3)\pi - m\delta$.
$4(3)\pi_1 = 34134\cdot38$; $4(3)\pi_2 = 34140\cdot30$.

λ, Intensity.	ν.	Δν.	*m*.	$m\delta_2$, $m\delta_1$.
§ — −5889·97 (3) −5891·65 (2)	— −16973·32 −16968·48		3 (2)	51108·78 51107·70

Combinations.

λ, Intensity.	ν.	Δν.
−2836·710 (10) −2837·602 (8)	−35241·75 −35230·69	11·06
1036·84 (5) 1036·22 (5)	96447 96505	58

Derivation of x, $2(1)\pi_1$ and $2(1)\pi_2$.

$\left.\begin{array}{l}3(2)\pi_1 - x\\ 3(2)\pi_2 - x\end{array}\right\}$ $x = 100164\cdot9$.

$\left.\begin{array}{l}2(1)\pi_1 - x\\ 2(1)\pi_2 - x\end{array}\right\}$ $\begin{array}{l}2(1)\pi_1 = 196612.\\ 2(1)\pi_2 = 196670.\end{array}$

§ Satellites not directly observed.

n = Diffuse.

r = Diffuse to red.

wave-lengths have been calculated, and it will be seen that there is a very satisfactory agreement with the observed values. The greatest divergence is in the line λ 533·9 for which, however, the mean of Simeon's and Millikan's values is in close agreement with the calculated position.

The Series Terms.

The series terms may be conveniently summarised as in Table IV. A few additional terms have been extrapolated from the known terms by formulæ calculated from the last two observed values in each series. Thus—

$$\left.\begin{array}{r} 39425\cdot 2 \\ 23310\cdot 8 \end{array}\right\} \quad m\sigma = 4\mathrm{N}\Big/\left(m + 0\cdot 345406 - \frac{0\cdot 028740}{m}\right)^2$$

$$\left.\begin{array}{r} 28534\cdot 7 \\ 18164\cdot 2 \end{array}\right\} \quad m\delta_1 = 4\mathrm{N}\Big/\left(m + 0\cdot 894946 + \frac{0\cdot 078348}{m}\right)^2$$

$$\left.\begin{array}{r} 17702\cdot 5 \\ 12282\cdot 8 \end{array}\right\} \quad m\phi = 4\mathrm{N}\Big/\left(m + 0\cdot 969307 + \frac{0\cdot 035580}{m}\right)^2$$

Calculated terms are shown in brackets.

Table IV.—Series Terms of C II.

Bohr's numbers.	2	3	4	5	6	7
mx	—	100165				
$m\sigma$	—	80121	39425	23311	(15387)	(10912)
$m\pi_2$	196670	64934	34140			
$m\pi_1$	196612	64923	34134			
$m\delta_2$	—	51108·9	28535·1	18164	(12558)	(9193)
$m\delta_1$	—	51107·6	28534·7			
$m\phi$	—	—	27680	17703	12283	(9017)
$4\mathrm{N}/m^2$	(109678)	(48746)	(27420)	(17549)	(12187)	(8953)

The corresponding "effective quantum numbers" are given in Table V, these being the values of the square root of 4N/T, where T is the term.

Table V.—Effective Quantum Numbers.

Bohr's numbers.	2	3	4	5	6	7
mx	—	2·092822				
$m\sigma$	—	2·340005	3·335826	4·338221	5·339658	6·340616
$m\pi_2$	1·493555	2·599281	3·584732			
$m\pi_1$	1·493775	2·599504	3·585043			
$m\delta_2$	—	2·929826	3·921030	4·914533	5·910616	6·908004
$m\delta_1$	—	2·929865	3·921062			
$m\phi$	—	—	3·981142	4·978202	5·976423	6·974237

It will be observed that the decimal parts of the numbers for the σ terms decrease from the first to the second, and afterwards increase, and that the π terms first show an increase and then a decrease. This is unusual, but occasionally occurs in connection with δ terms in other spectra.

Conclusions.

From the foregoing observations and calculations it is clear that the spectrum of ionised carbon consists of a doublet system, as would be expected from the spectroscopic displacement law. The spectrum would, in fact, be expected to be of the same type as that of the neutral atoms of boron, the element which precedes carbon in the periodic system. The series system of neutral boron has not yet been traced, but there is evidence to show that it consists of doublets,* like the spectra of other elements of the third group. The arrangement of the electronic orbits in neutral boron is not certainly known, but Bohr† has supposed that two of the three outer electrons are in 2_1 orbits and the third probably in a 2_2 orbit. The last named would be more loosely bound than the others, and the largest series term would accordingly be a p term corresponding with the subordinate (or azimuthal) quantum number 2. This view of the structure of the boron atom is in accordance with the series data for C II, from which it will be seen that the largest known term is 2π; the electron which produces the spectrum must therefore occupy a 2_2 orbit in the normal state of the ionised atom.

The value 196670 for the highest series limit of C II corresponds to a second ionisation potential of 24·28 volts, representing the energy necessary to remove the second electron when the first has already been removed. The first ionisation potential is not known, as the series of C I have not yet been worked out, but Saunders* has suggested that it may be from 7 to 8 volts.

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* 'Report on Series,' p. 155.

† 'Ann. d. Phys.,' vol. 71, p. 260 (1913).

Summary.

The production of previously unrecorded lines of carbon has led to the identification of the leading members of the series of ionised carbon (C II or C^+) in the ordinary region of observation. The main series, however, lie in the extreme ultra-violet and were identified in the observations of Simeon and Millikan with the aid of the spectral terms thus determined. The series of C II form a doublet system, like the spectra of boron and other elements of Group III, as would be expected from the spectroscopic displacement law. The highest terms are the common limits of the sharp and diffuse series, 196612 and 196670, from which it may be deduced that the second ionisation potential of carbon is 24·3 volts.

In the normal state of the atoms, two of the outermost electrons in ionised carbon probably move in 2_1 orbits, while the electron which generates the spectrum traverses a 2_2 orbit, as suggested by Bohr for neutral boron.

The author has pleasure in acknowledging the valuable assistance in the experimental work which has been given at different times by Mr. J. Brooksbank, Miss Saltmarsh, and Mr. E. W. H. Selwyn.

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Atmospheric Pollution and Potential Gradient at Kew Observatory, 1921 *and* 1922.

By C. Chree, Sc.D., LL.D., F.R.S., and R. E. Watson, B.Sc.

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§1. It has long been known that fog at Kew Observatory is usually associated with high values of the potential gradient of atmospheric electricity, and it was found some years ago[*] that the influence was not confined to thick fog, but prevailed to a greater or less extent in less opaque conditions of the atmosphere, diminishing as the opacity diminished. The introduction of one of Dr. Owens' pollution recorders has enabled a more complete investigation to be made of the influence of impurity of the atmosphere on the potential gradient. The pollution and potential records for two complete years, 1921 and 1922, are utilised.

Before proceeding further, a reference is necessary to the nature of the pollution records. The amount of impurity is determined by the blackening of a paper filter, through which a definite volume of atmospheric air has been drawn. The blackened area is compared optically with standard papers, and a pollution number 0, 1, 2, etc., is assigned accordingly. Two points call for particular notice. There is necessarily a considerable interval of pollution covered by any one pollution number, and in particular No. 0 does not really mean a total absence of pollution. The second point is that the assumption that a given darkening of the filter paper answers to a definite mass of dirt per unit volume of the atmosphere may be only an approximation to the truth. Conceivably, some dirt may, mass for mass, blacken the filter paper less than other dirt. The composition of the dirt in the atmosphere may vary throughout the year. There may, for instance, be differences in the sizes of dust particles, and the influence on the potential gradient may depend on the average size of the particle, as well as on the dirt mass per cubic metre. A minute knowledge of the composition of the dust may be essential to a complete study of its action. On the other hand, as will appear presently, the effect is not a small one, and it has appeared desirable to publish the results obtained without further delay.

§2. The investigation has been directed to two points: (1) the influence of atmospheric impurity on the mean absolute value of potential gradient, and

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[*] 'Roy. Soc. Proc.,' A, vol. 95, p. 210 (1919).

(2) the influence of the varying impurity throughout the day on the regular diurnal variation of potential gradient.

It has been the practice at Kew to confine the complete hourly measurements of the potential gradient curves derived from the Kelvin waterdropper to a limited number of days, usually 10 a month. The primary criterion for a selected day is the absence of negative potential. Usually negative potential is associated with rain. Sometimes, however, it occurs without rain, and sometimes rain, especially light rain, is unaccompanied by negative potential. Thus the selected days may be regarded as representative on the whole of fair weather conditions, but light rain occurred, no doubt, on a few of them. Another criterion in the selection of the days is the absence of notably inferior insulation in the electrograph. Occasionally in a rainy month it is impossible to get as many as 10 suitable days, and in one or two of the months included only nine days were available. When there is an ample choice of days the selection aims at representing fairly the earlier and later portions of the month, but when the choice is restricted this may be impossible. Pollution, on the other hand, has been measured on every hour of every day, unless the apparatus was out of action. To obtain strictly comparable results for the two elements from complete days, it was necessary either greatly to extend the potential gradient measurements, or else to compare the potential gradient results with pollution results derived from the same restricted number of days. In view of the other demands on our time, the latter course was adopted.

Whilst complete hourly measurements of potential gradient curves are made only for the selected days, it has been the practice of late years to measure the curves on all days at four fixed hours, viz. 3 h., 9 h., 15 h. and 21 h. G.M.T. There are usually a few failures in the course of a month in both the pollution and the potential curves. Thus, even for 3 h., 9 h., 15 h. and 21 h. it was seldom that all days of the month were available. Still, the days that had to be omitted from the comparison of the four hours were comparatively few.

§3. Table I deals mainly with the results obtained from the 10 selected days of each month of 1921 and 1922. The selected days of each month were divided into two groups, composed respectively of the five "clean" days, *i.e.* the five of the selected days having the lowest mean daily value of pollution, and the five "dirty," *i.e.* less clean, days. The mean quantities of pollution and the mean values of potential gradient were calculated separately for the two groups. To explain the entries in Table I, take, for example, December, 1921. In the first column we have 0·480, the mean mass (in milligrams per cubic metre) of dirt present in the atmosphere on all the days of the month for which the pollution record was complete. The values in the second and third columns, 0·343 and 0·623, are the corresponding mean values of the pollution for the five "clean" and the five "dirty" days composing the 10 days selected for measurements of potential gradient. The mean pollution for the selected days, 0·483, was in this case practically identical with the mean from all days of the month. So in this particular month the 10 selected days represented average pollution conditions extremely well. This was not always the case. For instance, in April, 1921, the selected days were, on the average, considerably more polluted than the average day of the month. On the whole, however, the selected days did very fairly represent average pollution conditions. In every case the five "clean" days were less dirty, usually much less dirty, than the average day of the month; and with the exception of May, 1922, the five "dirty" days were less clean, usually conspicuously less clean, than the average day of the month.

In Table I, as elsewhere in this paper, the year is divided into three 4-month seasons, viz. winter, including January, February, November and December; equinox, including March, April, September and October; and summer, including May to August.

Considering now the potential gradient results, we see that in 21 months out of the 24 the potential from the five "dirty" days was the higher of the two, and the excess was usually very substantial. The excess is clearly shown in all the seasons, and especially in winter, the season in which pollution has its highest values.

Even on the five "clean" days there is usually a very considerable amount of pollution. If the greater pollution on the five "dirty" days is the cause of their higher potential, it is reasonable to suppose that even on the five "clean" days the potential is higher than it would be if the air were quite pure. If we suppose that there is a linear relation between the increase of potential and the increase of dirt, a calculation can be made of what the potential would be on the ideal perfectly clean day. Thus, taking the results for the complete year 1921, as given in Table I, we have an increase of 90 volts associated with an increase of 0·249 in pollution. The representative 10 days give $\frac{1}{2}$ (235 + 325), or 280, as the potential gradient answering to a pollution of $\frac{1}{2}$ (·199 + ·448) or ·3235. Consequently the potential gradient answering to zero pollution is 280 − (90 × ·3235 ÷ ·249), *i.e.* 163 volts per metre. A similar calculation might have been made for each month from the data of that month alone. Theoretically this might have had advantages, because the nature of the pollution, or the extent of its influence, might depend on moisture

Table I.—Pollution and Potential Gradient on Selected " Clean " and " Dirty " Days.

Month or Season.	1921.						1922.						Potential Ideal—Mean.
	Pollution.			Potential.			Pollution.			Potential.			
	All days.	" Clean."	" Dirty."	" Clean."	" Dirty."	Ideal.	All days.	" Clean."	" Dirty."	" Clean."	" Dirty."	Ideal.	
				v/m	v/m	v/m				v/m	v/m	v/m	v/m
January	0·195	0·103	0·348	263	334	217	0·497	0·325	1·063	279	518	112	165
February	0·482	0·291	0·587	391	564	319	0·466	0·360	0·648	314	608	253	286
March	0·195	0·139	0·287	312	336	247	0·464	0·443	0·577	430	465	237	242
April	0·360	0·337	0·693	235	350	107	0·383	0·305	0·604	231	489	172	140
May	0·206	0·142	0·257	142	188	93	0·324	0·171	0·313	207	195	101	97
June	0·052	0·027	0·090	153	190	150	0·225	0·099	0·363	132	219	80	115
July	0·123	0·101	0·160	135	175	108	0·245	0·227	0·313	178	170	63	86
August	0·117	0·063	0·142	140	219	143	0·326	0·283	0·381	202	252	90	117
September	0·171	0·142	0·241	274	209	172	0·443	0·369	0·492	199	253	48	110
October	0·333	0·189	0·439	172	247	97	0·498	0·409	0·616	359	397	166	132
November	0·967	0·515	1·505	350	659	140	0·563	0·440	0·655	394	449	195	168
December	0·480	0·343	0·623	254	428	167	0·326	0·276	0·377	306	328	182	175
Year	0·307	0·199	0·448	235	325	163	0·397	0·309	0·534	269	362	141	152
Winter	0·531	0·313	0·766	315	496	211	0·463	0·350	0·686	323	476	186	198
Equinox	0·265	0·202	0·415	248	286	156	0·447	0·382	0·572	305	401	156	156
Summer	0·125	0·063	0·162	143	193	124	0·280	0·195	0·343	180	209	83	104

or other atmospheric conditions having a large seasonal variation. But the data for a single month depend on so small a number of days that accident must play a large part in the results. Unless pollution be the sole cause of the potential gradient, which seems hardly likely *a priori*, there will naturally in most months be a considerable difference between the five "clean" and the five "dirty" days in other respects than simply pollution. Thus, in calculating the potential gradient for the perfectly clean day in the individual months of the year, it seemed the best course to accept for the effect of pollution on potential gradient the result obtained for the year as a whole. In 1921, as already pointed out, a rise of 0·249 in pollution was associated with a rise of 90 v/m, *i.e.* the rise of potential gradient answering to 1·0 pollution was 361 v/m. In 1922 a rise of 0·225 in pollution was associated with a rise of 93 v/m, or the rise of potential gradient answering to 1·0 pollution was 413 v/m. These figures were used in calculating for the 12 months of each year the potential gradient for the ideal perfectly clean day. If, instead of treating the years separately, we took a mean from the two figures obtained above, or 387 v/m, as the equivalent of 1·0 pollution, we should get as the mean potential gradient for the ideal perfectly clean day 155 v/m in 1921, and 152 v/m in 1922. The similarity of these figures encourages the view that the enhanced values of potential gradient in 1922 as compared with 1921, apparent in all the seasons, resulted from the enhanced value of the pollution. It was 1921, not 1922, that was the exceptional year, the atmosphere being exceptionally clear in many months of the former year owing to the prolonged coal strike (April 1 to July 1). The mean value of the potential gradient for 1921 was the lowest recorded since 1902.

The figures in the last column of Table I suggest that the differences apparent between the values of the potential gradient at different seasons of the year are only partly due to differences in atmospheric pollution, and that summer values would be considerably lower than winter values even if the atmosphere were perfectly pure.

A point which should be duly noted is that the difference between the five "clean" and the five "dirty" days is usually much less than the difference between the most dirty and the cleanest day of the entire month.

§ 4. Table II summarises results for 1921 derived from the four hours at which potential gradient measurements are made on all days of the month. The days were grouped according to the pollution shade number recorded. In 1921, from June to October, the hole limiting the current of air drawn through the plug was reduced in size so as to concentrate the dirt on a smaller area, and so make the apparatus more sensitive. With the ordinary large hole, Dr. Owens

Table II.—Pollution Numbers and Potential Gradients, 1921, at Four Selected Hours.

Month. or Season.	3 h.					9 h.						15 h.					21 h.					
	Pollution.		Potential Gradient.			Pollution.		Potential Gradient.				Pollution.		Potential Gradient.			Pollution.		Potential Gradient.			
	A.	B.	0.	1	2	A.	B.	0.	1	2	3	A.	B.	0.	1	2	A.	B.	0.	1	2	3
			v/m	v/m	v/m			v/m	v/m	v/m	v/m			v/m	v/m	v/m			v/m	v/m	v/m	v/m
January	0·19	0·19	135	(320)	—	1·22	1·22	(155)	293	(595)	(498)	0·74	0·75	258	268	(572)	0·63	0·63	234	(389)	(439)	—
February	0·83	0·73	265	417	(380)	2·26	2·22	—	446	491	529	1·00	0·93	305	526	(663)	2·09	2·04	(280)	496	560	(637)
March	0·20	0·27	214	285	(150)	1·16	1·18	(237)	312	407	(751)	0·36	0·41	262	201	—	1·04	1·07	277	345	(444)	(369)
April	0·80	0·86	175	270	(292)	1·60	1·61	179	305	(410)	(534)	0·83	0·73	165	330	(363)	1·33	1·35	210	340	465	(410)
May	0·61	0·48	102	153	(83)	0·71	0·71	251	222	(253)	—	0·57	0·54	126	140	(405)	0·61	0·61	210	193	—	—
June*	0·46	0·60	114	142	(175)	0·61	0·63	173	232	(281)	—	0·29	0·30	132	205	(141)	0·64	0·66	155	182	(253)	—
July*	1·33	1·39	(105)	91	129	1·50	1·48	(168)	162	246	(279)	0·50	0·52	117	104	(307)	1·27	1·36	(181)	150	220	(363)
August*	1·29	1·33	(110)	130	148	1·32	1·38	—	172	265	(273)	0·97	1·00	(136)	115	(151)	1·23	1·28	(153)	161	193	(115)
September* ..	1·62	1·59	91	148	143	2·58	2·56	—	206	306	(257)	1·19	1·20	(42)	200	225	1·50	1·54	(184)	223	188	(138)
October* ..	3·52	3·31	(76)	174	—	5·15	5·26	—	(204)	(271)	(221)	1·33	1·33	(147)	190	221	3·44	3·52	(200)	(221)	(259)	329
November ..	1·70	1·66	(165)	246	395	3·87	3·57	(97)	(309)	413	(447)	3·30	3·34	(190)	528	(509)	3·43	3·48	(151)	(268)	491	(358)
December ..	0·97	1·00	(128)	187	(288)	1·94	1·94	—	248	388	(427)	1·61	1·61	—	266	371	1·65	1·67	(185)	268	381	(477)
Winter	0·92	0·90	180	241	366	2·32	2·24	138	310	446	476	1·66	1·66	282	323	506	1·95	1·95	230	364	466	510
March to May ..	0·54	0·54	174	213	222	1·16	1·17	228	280	372	(578)	0·59	0·56	189	223	(380)	0·99	1·01	230	239	456	—
June to October	1·64	1·64	105	139	143	2·23	2·26	172	196	271	258	0·86	0·87	124	164	225	1·62	1·67	164	179	210	292

* Small hole in use in pollution recorder.

found pollution figure 1 to answer to a dirt content of 0·32 milligram per cubic metre, while with the smaller hole the equivalent value was only 0·1 milligram per cubic metre. Thus the potential gradients associated with the different pollution figures in Table II for the months June to October are not comparable with the potential gradients in the same columns for the remaining seven months of 1921. The entry under A is the mean pollution scale figure—scale figures being treated as numerical quantities—derived from all the days for which the pollution record was complete. The entry under B is the corresponding mean figure derived from all the days for which both pollution and potential data were available. The close accordance of the A and B figures is evidence that the days available for the comparison of pollution and potential were fairly representative.

The number of days available for the calculation of the mean potentials for the several pollution numerals was very variable. Unless the days available exceeded five the result is enclosed in brackets. If only one or two days were available no result is given.

Table III for 1922 corresponds to Table II, but is more homogeneous, because the larger hole was used throughout the year. Pollution at Kew Observatory is normally much higher at 9 h. and at 21 h. than at 3 h. In most months of 1922, 3 h. was the only hour at which pollution figure 0 was adequately represented.

Even in individual months, when an adequate number of days was available, Tables II and III show few exceptions to the rule that the potential gradient increases with the pollution. In the seasonal data there is no exception to the rule, and the increase is usually substantial. As already remarked, pollution figure 0 does not really signify a total absence of pollution, but only that there was too small an effect on the filter paper to warrant figure 1. Thus the potentials associated with pollution figure 0 in Tables II and III are presumably somewhat in excess of those answering to perfect purity in the atmosphere. The nearest approach to perfect purity should answer to pollution figure 0 from June to October, 1921. Taking this season as a whole, the mean of the potentials under 0 in Table II at the four observation hours is 141 v/m. A mean from these four hours combined ought theoretically to approach closely to the true mean for the day. If we take a mean from the potentials given in Table I for the ideal pure days of the months June to October, 1921, we obtain 134 v/m. The difference between these two estimates is small, and is in the direction to be expected. This supports the view that so far as the influence of pollution on potential gradient is concerned, the days selected for hourly potential measurements are fairly representative.

Table III.—Pollution Numbers and Potential Gradients, 1922, at Four Selected Hours.

Month or Season.	3 h.					9 h.					15 h.					21 h.					
	Pollution.		Potential Gradient.			Pollution.		Potential Gradient.			Pollution.		Potential Gradient.			Pollution.		Potential Gradient.			
	A.	B.	0.	1	2	A.	B.	1	2	3	A.	B.	0.	1	2	A.	B.	0.	1	2	3
			v/m	v/m	v/m			v/m	v/m	v/m			v/m	v/m	v/m			v/m	v/m	v/m	v/m
January	0·68	0·80	167	304	(354)	1·64	1·67	342	460	(586)	1·82	1·88	—	327	415	2·25	2·37	—	244	439	(541)
February	0·81	0·68	157	314	(634)	1·85	1·87	308	402	(705)	1·38	1·38	—	296	(449)	1·96	1·96	—	311	530	640
March	0·94	0·97	170	240	(397)	1·77	1·80	323	456	495	1·35	1·33	—	296	541	1·84	1·96	—	408	525	583
April	0·68	0·76	115	195	(398)	1·46	1·55	269	390	(517)	1·07	1·05	(205)	199	(535)	1·46	1·56	(134)	241	586	(450)
May	1·00	1·04	(145)	175	(133)	1·16	1·17	260	302	—	0·58	0·58	167	177	—	1·06	1·06	(162)	242	288	—
June	0·53	0·53	103	176	(163)	1·00	1·00	190	(452)	—	0·67	0·65	143	134	(352)	0·73	0·72	162	211	(193)	—
July	0·68	0·67	102	141	—	0·90	0·90	200	(340)	—	0·74	0·73	105	125	(137)	0·84	0·84	191	205	(333)	—
August	0·97	0·90	158	155	(241)	1·24	1·24	278	(327)	(355)	0·90	0·88	(181)	158	—	1·10	1·10	—	247	(337)	—
September	1·25	1·28	(52)	160	138	1·64	1·67	231	271	(391)	1·21	1·21	—	182	(200)	1·57	1·50	—	225	279	(228)
October	1·11	1·06	(209)	252	(284)	2·22	2·17	293	396	522	1·15	1·17	(272)	389	482	1·85	1·89	—	395	465	456
November	1·43	1·35	(248)	310	446	2·13	2·04	408	460	(512)	1·70	1·71	—	336	468	2·13	2·08	—	475	391	(440)
December	0·50	0·52	131	223	—	1·37	1·39	329	415	—	1·10	1·11	—	325	(544)	1·13	1·14	—	387	(517)	—
Year	0·86	0·88	—	—	—	1·53	1·54	—	—	—	1·14	1·14	—	—	—	1·49	1·51	—	—	—	—
Winter	0·85	0·84	156	285	447	1·75	1·74	340	437	613	1·50	1·52	—	320	453	1·87	1·89	—	359	447	568
Equinox	1·00	1·02	141	213	279	1·77	1·80	273	391	492	1·19	1·19	227	278	463	1·68	1·73	—	305	441	470
Summer	0·79	0·79	116	160	167	1·08	1·08	155	230	343	0·72	0·71	145	149	304	0·93	0·93	171	228	295	—

§ 5. Tables IV and V give the diurnal inequalities of pollution for the five "clean" and the five "dirty" days, 1921 and 1922 being combined. The algebraically largest and least of the hourly values are in heavy type. The results for the year as a whole are shown graphically in fig. 1 (p. 326).

The amount of pollution varies much from day to day, and even in the course of a single day large changes occur through shifting of the wind or varying incidence of heavy fog. There must thus be a considerable accidental element in an equality based, like the monthly inequalities of Tables IV and V, on only 10 days. In most, if not all cases, there is a decided double oscillation. On "clean" days the principal maximum occurs in the forenoon in the inequalities for the year, the three seasons, and 10 months out of the 12, September and November being the exceptions. On "dirty" days the principal maximum is seen in the forenoon from April to November, but in the afternoon from December to March. It occurs in the forenoon in equinox and summer, but in the afternoon in winter and in the year as a whole. The forenoon would seem to be the normal time of occurrence of the principal maximum, but with increasing dirt there is a distinct tendency for the maximum to pass to the afternoon, especially in winter. This feature will be recognised in fig. 1.

The hour of the principal minimum seems largely dependent on the season of the year. In both the "clean" and the "dirty" days it appears in the morning from November to March, but in the afternoon from May to September. April and October have their principal minimum in the morning on "clean" days, but in the afternoon on "dirty" days. In the inequalities for the year and the winter season the principal minimum is in the morning for both "clean" and "dirty" days. In summer, on the other hand, both classes of days have the principal minimum in the afternoon. In equinox the principal minimum is in the morning on "clean" days, but in the afternoon on "dirty" days. On the whole, then, it would appear that increasing dirt tends to throw both the principal minimum and the principal maximum into the afternoon, the minimum preceding the maximum. A minimum in pollution naturally represents a gradual purification of the atmosphere taking place during the hours when the actual dirt production is comparatively small. Anything which tends to increase the afternoon maximum of pollution, as compared with the forenoon maximum, will naturally prejudice the early morning minimum as compared with the afternoon minimum.

§ 6. Tables VI and VII give the diurnal inequalities of potential gradient for the "clean" and the "dirty" days, combining the two years 1921 and 1922. In both "clean" and "dirty" days the principal maximum appears in the

Table IV.—Diurnal Inequality of Atmospheric Pollution

Hour G.M.T.	1	2	3	4	5	6	7	8	9	10	11
January	−0·072	−0·071	−0·149	**−0·187**	−0·186	−0·104	−0·022	+0·099	+0·141	**+0·183**	+0·144
February	−0·197	−0·261	**−0·293**	**−0·293**	**−0·293**	−0·133	−0·005	+0·219	**+0·251**	+0·187	+0·219
March	−0·131	**−0·163**	**−0·163**	−0·131	**−0·168**	−0·085	+0·093	**+0·189**	**+0·189**	+0·093	−0·003
April	−0·041	−0·009	−0·102	**−0·131**	+0·032	+0·099	+0·099	**+0·103**	+0·074	−0·019	−0·048
May	+0·039	+0·040	+0·042	+0·043	+0·081	**+0·189**	+0·155	+0·120	+0·087	−0·019	−0·017
June	−0·037	−0·045	−0·034	−0·012	**+0·063**	+0·045	+0·036	+0·047	+0·049	+0·060	0·000
July	+0·005	+0·034	+0·022	+0·040	+0·028	+0·067	**+0·107**	+0·065	+0·053	+0·008	+0·028
August	−0·025	−0·015	+0·017	+0·007	+0·047	+0·047	+0·037	+0·027	**+0·059**	+0·037	+0·037
September	−0·023	−0·021	−0·020	−0·018	−0·006	−0·026	+0·079	+0·059	+0·009	−0·009	−0·028
October	−0·109	**−0·139**	−0·126	−0·124	−0·099	+0·010	+0·160	+0·149	**+0·244**	+0·184	+0·021
November	−0·157	−0·157	−0·125	−0·157	**−0·189**	−0·093	−0·125	+0·035	+0·067	+0·067	+0·035
December	−0·056	−0·090	−0·093	**−0·160**	−0·131	−0·138	−0·008	+0·054	**+0·179**	+0·080	+0·077
Year	−0·067	−0·075	−0·085	**−0·094**	−0·068	−0·006	+0·051	+0·097	**+0·117**	+0·071	+0·039
Winter	−0·121	−0·145	−0·165	−0·199	**−0·200**	−0·116	−0·040	+0·102	**+0·159**	+0·129	+0·119
Equinox	−0·076	−0·088	**−0·103**	−0·101	−0·059	+0·012	+0·108	+0·125	**+0·129**	+0·062	−0·015
Summer	−0·004	+0·004	+0·012	+0·019	+0·055	**+0·087**	+0·084	+0·065	+0·062	+0·022	+0·012

Table V.—Diurnal Inequality of Atmospheric Pollution

Hour G.M.T.	1	2	3	4	5	6	7	8	9	10	11
January	−0·361	−0·337	−0·377	−0·417	**−0·425**	−0·360	−0·313	−0·120	−0·105	−0·017	+0·007
February	−0·128	−0·159	−0·230	**−0·265**	**−0·265**	−0·194	−0·052	+0·161	+0·232	+0·197	+0·161
March	−0·088	−0·160	−0·168	**−0·208**	−0·088	−0·082	+0·120	+0·240	+0·136	+0·064	−0·008
April	−0·087	−0·118	−0·073	−0·068	+0·002	+0·138	+0·239	**+0·440**	+0·317	+0·070	−0·052
May	−0·084	−0·054	−0·023	+0·040	+0·070	+0·101	+0·100	**+0·130**	+0·097	+0·064	−0·002
June	+0·013	+0·047	+0·044	+0·076	+0·073	+0·117	**+0·185**	+0·147	+0·080	−0·035	−0·002
July	−0·047	−0·023	−0·002	+0·010	+0·064	+0·138	**+0·161**	+0·037	+0·029	+0·021	+0·002
August	−0·028	+0·056	+0·028	+0·021	+0·062	+0·060	**+0·111**	+0·078	+0·014	+0·003	−0·009
September	−0·036	−0·039	−0·004	−0·006	−0·022	+0·028	+0·077	**+0·140**	+0·110	+0·069	+0·030
October	+0·034	−0·002	−0·068	−0·040	−0·014	−0·017	+0·093	+0·237	**+0·253**	+0·058	−0·075
November	−0·128	−0·282	−0·336	−0·344	**−0·416**	−0·392	−0·336	−0·120	+0·064	+0·280	**+0·336**
December	−0·212	**−0·244**	−0·212	−0·148	−0·180	−0·180	−0·052	−0·020	+0·108	+0·172	+0·076
Year	−0·096	−0·105	**−0·119**	−0·112	−0·095	−0·050	+0·028	+0·112	+0·112	+0·078	+0·040
Winter	−0·206	−0·248	−0·289	−0·293	**−0·322**	−0·284	−0·188	−0·027	+0·075	+0·158	+0·145
Equinox	−0·044	−0·079	−0·078	−0·081	−0·031	+0·029	+0·132	**+0·264**	+0·204	+0·064	−0·026
Summer	−0·037	+0·006	+0·010	+0·037	+0·067	+0·104	**+0·139**	+0·098	+0·056	+0·013	−0·008

Table VI.—Diurnal Inequality of Potential

Hour G.M.T.	1	2	3	4	5	6	7	8	9	10	11
January	− 63	− 86	− 88	− 99	− 98	−111	− 80	− 29	+ 5	+ 38	+ 38
February	− 84	− 89	−122	−108	− 92	− 69	− 36	− 8	+ 20	+ 36	+ 31
March	− 91	−118	−114	−118	− 96	− 69	− 2	+ 58	+ 37	+ 30	+ 15
April	− 55	− 54	− 56	− 61	− 32	− 11	+ 81	+ 91	+ 57	+ 32	+ 8
May	+ 5	− 12	− 18	− 29	− 24	+ 10	+ 71	+ 71	+ 46	+ 2	− 9
June	− 35	− 25	− 23	− 13	− 9	0	+ 20	+ 24	+ 19	+ 2	− 4
July	− 16	− 28	− 20	− 25	− 14	+ 36	+ 71	+ 47	+ 36	+ 10	− 1
August	− 20	− 35	− 39	− 25	− 5	+ 27	+ 69	+ 57	+ 89	− 1	− 4
September	− 41	− 62	− 73	− 62	− 59	− 22	+ 57	+ 64	+ 59	+ 29	+ 8
October	− 76	− 92	− 99	− 98	− 90	− 51	− 36	+ 6	+ 53	+ 49	+ 61
November	− 45	− 87	−101	− 86	− 86	− 62	− 17	+ 34	+ 78	+ 55	+ 39
December	− 47	−106	−124	−114	−107	− 94	− 43	+ 4	+ 61	+ 72	+ 55
Year	− 46	− 66	− 73	− 70	− 59	− 85	+ 13	+ 35	+ 42	+ 30	+ 20
Winter	− 60	− 92	−109	−102	− 96	− 84	− 44	0	+ 40	+ 50	+ 41
Equinox	− 66	− 80	− 86	− 85	− 69	− 38	+ 25	+ 55	+ 51	+ 35	+ 23
Summer	− 14	− 25	− 25	− 23	− 13	+ 18	+ 58	+ 50	+ 35	+ 3	− 5

on "Clean" Days. Unit 1 milligram per cubic metre.

12	13	14	15	16	17	18	19	20	21	22	23	24	Range.	Daily Mean.
+0·026	+0·028	−0·011	+0·031	+0·078	+0·074	+0·116	+0·038	+0·079	+0·041	−0·037	−0·116	−0·114	0·370	0·214
+0·123	+0·059	−0·069	−0·060	−0·087	+0·059	+0·187	+0·219	+0·155	+0·091	+0·059	−0·005	−0·165	0·544	0·325
−0·035	−0·035	−0·035	−0·035	+0·029	+0·093	+0·157	+0·189	+0·061	+0·061	−0·003	−0·099	−0·131	0·352	0·291
−0·045	−0·045	−0·041	−0·006	−0·067	+0·032	−0·029	+0·007	+0·103	−0·022	+0·045	+0·080	−0·077	0·234	0·291
−0·087	−0·086	−0·119	−0·118	−0·116	−0·151	−0·149	−0·112	−0·004	−0·003	+0·035	+0·036	+0·103	0·340	0·158
−0·063	−0·052	−0·050	−0·027	−0·025	+0·008	+0·009	+0·011	−0·010	+0·044	+0·003	−0·007	−0·016	0·126	0·063
+0·016	−0·008	−0·010	−0·023	−0·089	−0·133	−0·093	−0·064	−0·046	−0·006	+0·002	+0·031	−0·035	0·240	0·164
+0·007	−0·025	−0·067	−0·037	−0·057	−0·047	−0·015	−0·015	−0·015	+0·017	+0·007	−0·003	−0·035	0·126	0·173
−0·036	−0·034	−0·043	−0·041	+0·003	−0·027	+0·058	+0·060	+0·084	+0·044	−0·029	−0·017	−0·025	0·127	0·256
−0·027	−0·037	−0·104	−0·112	−0·057	+0·010	+0·074	+0·139	+0·078	−0·014	−0·001	+0·001	−0·070	0·383	0·299
−0·061	−0·029	+0·003	+0·035	+0·067	+0·067	+0·195	+0·099	+0·163	+0·195	+0·090	+0·035	−0·061	0·384	0·477
+0·011	+0·009	+0·006	+0·003	0·000	+0·094	+0·091	+0·057	+0·022	+0·051	−0·016	−0·018	−0·021	0·339	0·309
−0·014	−0·025	−0·045	−0·033	−0·023	+0·007	+0·050	+0·052	+0·056	+0·042	+0·014	−0·007	−0·054	0·211	0·252
+0·025	+0·017	−0·018	0·000	+0·026	+0·078	+0·147	+0·108	+0·105	+0·094	+0·026	−0·026	−0·090	0·359	0·331
−0·036	−0·050	−0·056	−0·048	−0·023	+0·027	+0·065	+0·099	+0·082	+0·017	+0·003	−0·009	−0·076	0·232	0·284
−0·032	−0·043	−0·061	−0·051	−0·072	−0·031	−0·062	−0·045	−0·019	+0·013	+0·012	+0·014	+0·005	0·168	0·140

on "Dirty" Days. Unit 1 milligram per cubic metre.

12	13	14	15	16	17	18	19	20	21	22	23	24	Range.	Daily Mean.
−0·001	+0·055	−0·049	+0·167	+0·511	+0·567	+0·591	+0·615	+0·543	+0·343	+0·015	−0·185	−0·321	1·040	0·705
+0·019	−0·017	−0·123	−0·128	−0·088	−0·052	+0·055	+0·126	+0·282	+0·303	+0·161	+0·055	−0·017	0·568	0·621
−0·080	−0·088	−0·160	−0·136	−0·144	−0·056	+0·064	+0·152	+0·208	+0·296	+0·128	+0·088	−0·080	0·504	0·432
−0·111	−0·135	−0·225	−0·281	−0·148	−0·174	−0·070	−0·001	+0·136	+0·141	+0·114	−0·004	−0·063	0·721	0·649
−0·003	−0·036	−0·038	−0·071	−0·040	−0·010	−0·043	−0·044	+0·050	+0·017	−0·048	−0·114	−0·051	0·244	0·259
−0·077	−0·044	−0·107	−0·050	−0·066	−0·105	−0·108	−0·086	−0·054	−0·057	−0·002	+0·031	−0·018	0·293	0·241
−0·016	−0·056	−0·033	−0·063	+0·013	−0·049	−0·026	−0·056	−0·022	+0·010	−0·001	−0·041	−0·039	0·224	0·236
−0·020	−0·021	−0·013	−0·014	−0·080	−0·069	−0·060	−0·020	−0·041	−0·013	−0·004	−0·006	−0·037	0·191	0·262
−0·001	−0·029	−0·056	−0·046	−0·024	−0·079	−0·042	−0·073	+0·005	+0·043	0·000	−0·003	−0·033	0·219	0·366
−0·289	−0·323	−0·337	−0·311	−0·179	+0·005	+0·135	+0·204	+0·190	+0·154	+0·130	+0·096	+0·070	0·580	0·527
+0·200	−0·032	−0·040	−0·016	+0·040	+0·224	+0·184	+0·208	+0·200	+0·224	+0·248	+0·176	+0·008	0·752	1·080
−0·020	−0·020	+0·012	+0·044	+0·076	+0·300	+0·268	+0·172	+0·172	+0·076	+0·012	+0·012	−0·212	0·544	0·500
−0·033	−0·062	−0·007	−0·075	−0·011	+0·042	+0·079	+0·100	+0·135	+0·128	+0·063	+0·009	−0·066	0·254	0·490
+0·050	−0·004	−0·050	+0·018	+0·135	+0·260	+0·274	+0·280	+0·337	+0·236	+0·109	+0·014	−0·135	0·609	0·726
−0·120	−0·144	−0·192	−0·194	−0·124	−0·076	+0·022	+0·070	+0·135	+0·158	+0·093	+0·044	−0·026	0·458	0·494
−0·029	−0·039	−0·048	−0·050	−0·043	−0·058	−0·059	−0·052	−0·017	−0·011	−0·014	−0·033	−0·036	0·198	0·250

Gradient on "Clean" Days (volts per metre).

12	13	14	15	16	17	18	19	20	21	22	23	24	Range.	Daily Mean.
+ 48	+ 27	− 2	+ 22	+ 24	+ 44	+ 87	+ 93	+ 87	+ 84	+ 59	+ 14	− 14	203	271
+ 44	+ 27	+ 14	− 5	− 13	+ 35	+109	+109	+103	+ 86	+ 42	− 11	− 16	231	353
+ 6	− 7	− 2	+ 1	+ 39	+ 44	+ 72	+ 64	+111	+111	+ 34	− 4	− 55	229	371
− 13	− 22	− 27	− 32	− 20	+ 14	+ 2	+ 87	+ 47	+ 43	+ 24	− 20	− 32	152	283
− 14	− 25	− 31	− 40	− 38	− 24	− 25	− 8	+ 17	+ 23	+ 21	+ 23	+ 6	111	175
+ 6	− 11	− 15	− 20	− 6	− 16	− 13	+ 20	+ 44	+ 32	+ 11	+ 13	− 8	69	143
− 18	− 26	− 39	− 40	− 35	− 23	− 29	− 3	+ 25	+ 33	+ 42	+ 19	− 2	111	156
− 9	− 35	− 39	− 39	− 44	− 37	− 24	+ 9	+ 35	+ 54	+ 37	+ 27	+ 4	113	171
− 11	− 24	− 19	+ 2	− 8	+ 5	+ 27	+ 38	+ 51	+ 49	+ 26	− 2	− 33	137	237
+ 18	+ 7	− 3	− 6	− 5	+ 47	+ 84	+106	+ 94	+ 57	+ 29	− 6	− 47	205	266
+ 46	+ 32	+ 14	+ 23	+ 22	+ 32	+ 38	+ 32	+ 19	+ 18	+ 17	+ 12	− 20	174	372
+ 58	+ 21	+ 22	+ 22	+ 50	+ 50	+ 52	+ 61	+ 62	+ 43	+ 36	+ 4	− 32	196	280
+ 13	− 3	− 11	− 9	− 3	+ 14	+ 32	+ 46	+ 53	+ 53	+ 36	+ 6	− 21	131	252
+ 49	+ 27	+ 12	+ 16	+ 21	+ 40	+ 72	+ 73	+ 68	+ 57	+ 39	+ 5	− 20	132	319
0	− 12	− 13	− 9	+ 2	+ 27	+ 46	+ 61	+ 76	+ 65	+ 41	− 8	− 41	162	277
− 9	− 24	− 31	− 35	− 30	− 25	− 23	+ 5	+ 30	+ 36	+ 28	+ 20	0	93	161

Table VII.—Diurnal Inequality of Potential

Hour G.M.T.	1	2	3	4	5	6	7	8	9	10	11
January	−106	**−139**	−111	−119	−116	− 91	− 21	+ 55	+ 90	+102	+ 52
February	− 52	−118	−150	−145	−135	**−174**	−156	− 74	+ 20	+ 56	+ 51
March	− 68	− 88	−108	**−143**	−127	− 74	− 29	+ 58	+ 86	+ 67	+ 44
April	− 81	− 99	−121	**−133**	− 78	− 51	− 8	+ 79	+ 92	+ 86	+ 5
May	− 36	− 57	**− 67**	− 57	− 85	+ 3	+ 40	+ 49	+ 45	+ 80	+ 2
June	− 22	− 42	− 60	− 60	− 52	+ 15	+ 84	**+127**	+110	+ 65	+ 16
July	**− 46**	− 40	− 42	− 35	− 15	+ 86	**+ 90**	+ 90	+ 77	+ 40	+ 10
August	− 53	**− 82**	− 67	− 54	− 13	+ 30	+ 39	**+ 69**	+ 67	+ 50	− 2
September	− 57	**− 76**	− 68	− 59	− 25	+ 5	+ 31	+ 57	**+ 74**	+ 53	+ 27
October	− 18	− 33	− 66	**− 90**	− 67	− 52	− 40	+ 18	+ 80	+ 73	− 15
November	− 26	− 87	− 47	− 67	−103	−101	**−108**	− 49	− 22	− 7	+ 46
December	−141	−136	**−144**	−141	−124	− 93	− 52	+ 15	+ 56	+ 68	+ 51
Year	− 59	− 83	− 88	**− 92**	− 74	− 45	− 11	+ 41	+ 65	+ 57	+ 24
Winter	− 81	**−120**	−113	−118	−119	−115	− 83	− 13	+ 36	+ 55	+ 50
Equinox	− 56	− 74	− 91	**−106**	− 74	− 48	− 12	+ 53	**+ 83**	+ 70	+ 15
Summer	− 39	− 55	**− 59**	− 51	− 29	+ 21	+ 63	**+ 84**	+ 75	+ 46	+ 7

afternoon in the case of the year and the winter season, but in the forenoon in the summer season. In equinox the afternoon maximum is decidedly the larger on "clean" days, but on "dirty" days the forenoon maximum is slightly the larger. On the "dirty" days the principal maximum appears in the forenoon in the four consecutive months June to September, but in the remaining eight months it appears in the afternoon. On the "clean" days there are only five months, including the three consecutive months January, February and March, which have the principal maximum in the afternoon.

On "dirty" days the principal minimum appears in the morning in every month except June, when the afternoon minimum is slightly the more prominent. On "clean" days the principal minimum is also in the forenoon from September to April, and in the inequalities for the year, winter and equinox; but in May, July and August and in the summer season it appears in the early afternoon.

The type of the diurnal inequality of potential gradient seems considerably dependent on the season of the year, but comparatively little on the greater or less amount of atmospheric pollution.

The principal points of agreement and difference between the diurnal inequalities of pollution and potential gradient for the three seasons are summarised below, (c) representing the "clean" and (d) the "dirty" days :—

Season.	Points of agreement.	Points of difference.
Winter ..	Max. (d) in afternoon Min. (c and d) in early morning	Max. (c) of pollution if anything in forenoon. Max. (c) of potential clearly in afternoon.

Gradient on " Dirty " Days (volts per metre).

12	13	14	15	16	17	18	19	20	21	22	23	24	Range.	Daily Mean.
+ 44	+ 40	+ 69	+ 40	− 1	+ 78	+ 94	+118	+ 91	− 20	− 39	− 80	− 74	252	426
+ 82	+ 20	− 2	+ 30	+ 33	+ 92	+141	+130	+130	+115	+ 86	+ 74	− 5	315	586
+ 20	− 6	− 35	− 32	− 17	+ 6	+ 73	+110	+115	+ 97	+ 51	+ 20	− 16	258	400
+ 8	− 70	− 77	− 48	+ 28	+ 19	+ 56	+ 80	+118	+125	+ 76	+ 37	− 38	258	420
− 13	− 15	− 14	− 18	− 9	− 4	− 1	+ 60	+ 59	+ 39	+ 26	− 13	− 15	127	192
− 34	− 51	− 56	− 65	− 31	+ 4	+ 34	+ 25	+ 11	− 3	+ 12	− 17	− 11	192	205
+ 3	− 5	− 16	− 24	− 28	− 26	− 17	− 22	− 8	+ 7	+ 13	− 7	− 32	136	172
− 13	− 23	− 13	− 32	− 4	− 7	+ 16	+ 88	+ 41	+ 44	+ 29	− 13	− 47	151	286
− 5	− 11	+ 11	+ 21	+ 8	+ 3	+ 7	+ 48	+ 44	+ 6	− 11	− 38	− 47	150	281
− 40	− 34	− 47	− 16	+ 49	+102	+ 98	+ 75	+ 31	+ 23	− 7	− 11	− 13	192	322
+ 61	+ 45	+ 40	+ 91	+114	+106	+ 71	+ 53	+ 14	+ 14	+ 1	− 5	− 38	217	554
+ 27	+ 25	+ 28	+ 26	+ 71	+104	+117	+110	+ 87	+ 57	+ 43	+ 15	− 67	261	378
+ 8	− 7	− 9	− 2	+ 17	+ 40	+ 58	+ 68	+ 61	+ 42	+ 23	+ 1	− 34	160	343
+ 41	+ 33	+ 34	+ 47	+ 55	+ 95	+106	+101	+ 80	+ 42	+ 28	+ 18	− 46	226	466
− 4	− 30	− 37	− 19	+ 16	+ 33	+ 59	+ 78	+ 77	+ 63	+ 27	+ 2	− 29	189	343
− 14	− 23	− 25	− 35	− 18	− 9	+ 8	+ 25	+ 26	+ 22	+ 20	− 12	− 26	148	201

Season.	Points of agreement.	Points of difference.
Equinox..	Max. (*d*) in forenoon Min. (*c*) in morning	Max. (*c*) of potential in afternoon. Max. (*c*) of pollution in forenoon. Min. (*d*) of potential in morning. Min. (*d*) of pollution in afternoon.
Summer ..	Max. (*c* and *d*) in forenoon Min. (*c*) in afternoon	Min. (*d*) of potential in morning. Min. (*d*) of pollution in afternoon.

In the above statement maximum stands for principal maximum, and minimum for principal minimum.

It would appear that an increase of pollution in the forenoon tends to bring the principal maximum of potential gradient into the forenoon, while a diminution of pollution in the afternoon tends to bring the principal minimum of potential gradient into the afternoon.

§ 7. The influence of increasing pollution on the amplitude of the regular diurnal variation of potential gradient is best studied in conjunction with the corresponding effect on the mean absolute value. Table VIII aims at supplying the more salient facts bearing on this point.

The pollution present on the " dirty " days was, taking the year as a whole, nearly double that present on the " clean " days, the ratio being distinctly greater in winter than in the other seasons. The corresponding increase in the absolute value of the potential gradient was also decidedly largest in winter, but was much smaller proportionately than for pollution. In winter and equinox the amplitude of the diurnal variation of pollution showed a large increase with the increase of pollution, but in summer the increase in the amplitude of the diurnal variation was relatively much less. The small size of the

Table VIII.—Ratios of Pollution and Potential Gradient Amplitudes Compared.

Nature of Ratio.	Element or Type of Day.	Pollution.				Potential Gradient.			
		Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.
"Dirty" day value / "Clean" day value	Mean daily value ..	1·94	2·19	1·75	1·79	1·36	1·52	1·24	1·25
	Diurnal Inequality range	1·20	1·70	1·97	1·18	1·22	1·24	1·17	1·56
Inequality range / Mean daily value	On "clean" days ..	0·84	1·08	0·82	1·20	0·52	0·57	0·58	0·57
	On "dirty" days ..	0·52	0·84	0·93	0·79	0·47	0·47	0·55	0·71

increase in the amplitude of the diurnal variation of pollution for the year as a whole was due to an increased seasonal variability in the type of the inequality. With increased pollution there was a very decided increase in the amplitude of the diurnal variation of potential gradient; but, except in summer, this increase was less proportionally than the increase in the absolute value itself. Table VIII also shows that, expressed in terms of the mean absolute value of the element, the amplitude of the diurnal variation is generally reduced by increase of pollution; but to this rule potential gradient in summer is a decided exception. The amplitude of the diurnal inequality expressed as a fraction of the mean absolute value is in every case less for potential gradient than for pollution.

§8. In a manufacturing neighbourhood there will naturally be a marked difference in the incidence of pollution on Sundays and on week-days, and if potential gradient is dependent on pollution a corresponding difference will naturally present itself in the case of potential gradient. Table IX compares pollution results from Sundays and from all days (including Sundays) at Kew; a non-cyclic correction has been applied. The values answering to the forenoon maximum are in heavy type, whether it is a principal maximum or not. All principal maxima and minima are also in heavy type. The comparison is limited to 1921. For reasons connected with the prolonged

Table IX.—Diurnal Inequality of Pollution, 1921,

Hour G.M.T.	1	2	3	4	5	6	7	8	9	10	11
January to June—											
Sundays	−0·091	**−0·123**	−0·093	−0·107	−0·107	−0·081	−0·010	+0·074	**+0·113**	+0·106	+0·072
All days	−0·089	−0·102	**−0·103**	−0·096	−0·066	−0·007	+0·062	**+0·138**	+0·131	+0·118	+0·087
July to December—											
Sundays	−0·057	−0·050	**−0·068**	−0·079	−0·080	−0·077	**−0·100**	−0·076	+0·008	+0·068	**+0·084**
All days	−0·061	−0·084	**−0·093**	−0·083	−0·078	−0·045	+0·008	+0·061	**+0·121**	+0·110	+0·083
Year—											
Sundays	−0·074	−0·086	−0·080	**−0·093**	**−0·093**	−0·079	−0·056	−0·001	+0·061	**+0·090**	+0·068
All days	−0·075	−0·093	**−0·098**	−0·090	−0·072	−0·026	+0·035	+0·100	**+0·126**	+0·114	+0·080

coal strike the earlier months of that year were much cleaner than the later months. Thus the first and second six months were considered separately, as well as in conjunction. In every one of the first six months pollution was lower at the second than at the first Sunday midnight, and usually to a notable extent, whereas in the second six months the reverse was true of every month except October. The large non-cyclic corrections thus entailed do not prejudice the mean values, but they do introduce an undesirable element of uncertainty into the diurnal inequalities. In each case the mean pollution for the Sundays is the higher, but the differences are so small that no significance attaches to the fact. A single bad fog falling on a Sunday would exert a decided effect on the results of one year.

Both half-years show the two following phenomena: The principal maximum is in the afternoon on Sundays, though in the forenoon on all days, but the difference between the forenoon and afternoon Sunday maxima is comparatively small. The forenoon maximum is later on Sundays than on all days.

The second result at least may well be true generally, as the hours of lighting domestic fires and cooking breakfast tend to be later on Sundays than on week days.

In view of the comparatively small difference between the pollution results for Sundays and all days, and the small number of Sundays amongst selected days, it did not seem worth while investigating specially the diurnal inequality of potential gradient on Sundays. This, however, should be done when several years' pollution data have accumulated.

§9. Fig. 1 shows graphically the diurnal inequalities of pollution and potential gradient for the whole year for the "clean" and "dirty" days as given in Tables IV to VII. The range of the inequality is obviously increased in both cases by the increase of pollution. In the case of pollution, the range of the afternoon oscillation is much more increased than that of the forenoon oscillation. In the case of potential the increase of pollution seems to reduce the

Sundays and all Days. Unit 1 milligram per cubic metre.

12	13	14	15	16	17	18	19	20	21	22	23	24	Mean.	Range.
+0·044	+0·027	−0·054	−0·005	+0·029	+0·048	+0·122	+0·064	+0·090	+0·054	−0·010	−0·064	−0·104	0·257	0·245
−0·005	−0·036	−0·061	−0·056	−0·038	−0·011	+0·036	+0·064	+0·081	+0·069	+0·022	−0·018	−0·070	0·248	0·241
+0·048	+0·008	+0·004	−0·012	+0·023	+0·063	+0·084	+0·072	+0·062	+0·084	+0·063	+0·014	−0·040	0·384	0·184
+0·037	−0·002	−0·021	−0·037	−0·014	+0·016	+0·035	+0·037	+0·029	+0·030	+0·015	−0·008	−0·048	0·365	0·214
+0·047	+0·014	−0·025	−0·009	+0·026	+0·055	+0·103	+0·068	+0·076	+0·069	+0·027	−0·025	−0·072	0·321	0·196
+0·018	−0·019	−0·041	−0·047	−0·026	+0·002	+0·036	+0·060	+0·055	+0·049	+0·018	−0·018	−0·059	0·307	0·224

time interval between the forenoon and afternoon maxima, retarding the former and accelerating the latter.

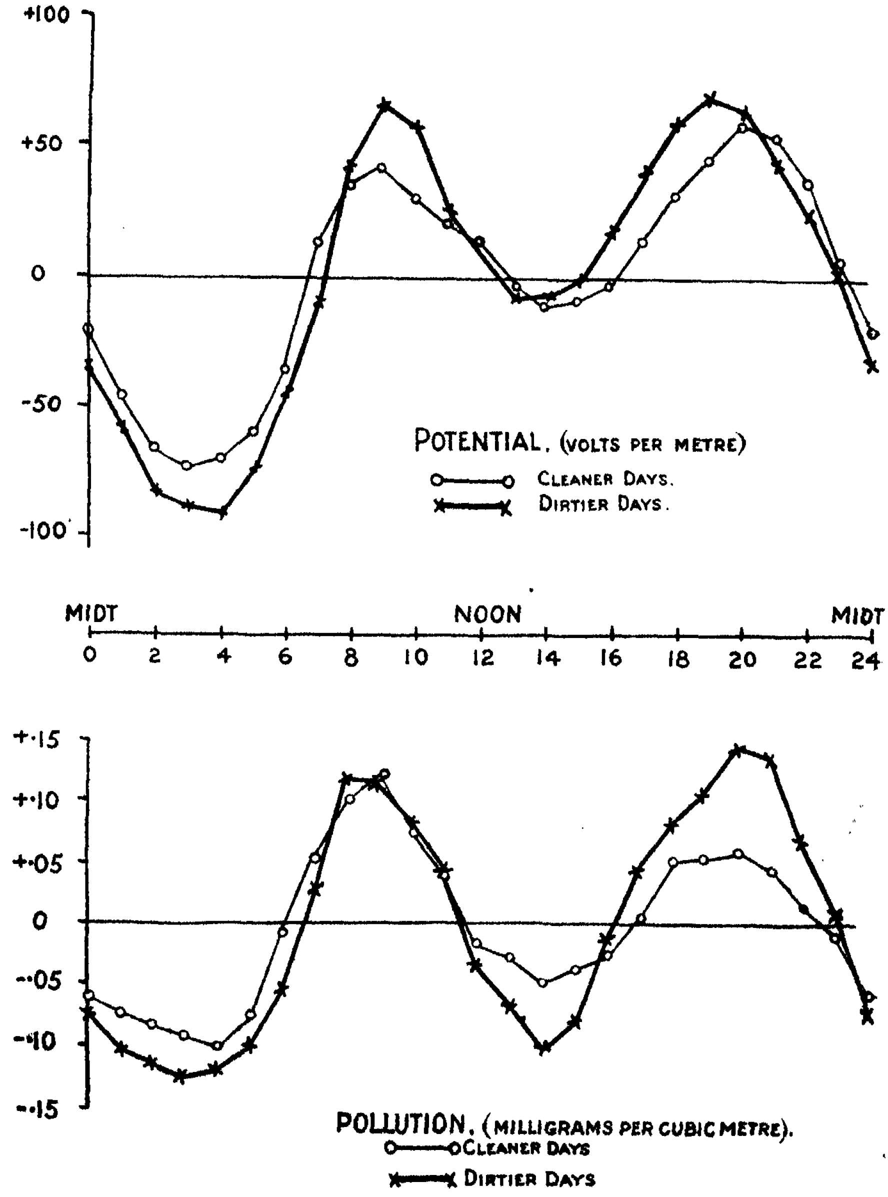

FIG. 1.—Diurnal Inequalities.

Figs. 2 and 3 illustrate the great variability in the amount of pollution in different days in the same season of the year and the consequent effects on the potential. The base line answers to the zero value of the element, whether pollution or potential.* The summer of 1921 was, of course, exceptionally clean as a whole, but days as clean as any of the selected days of that summer may be expected in other summers. In the ordinary winter, some individual days may be expected to have a pollution several times as great as that of the average "dirty" day of winter 1922.

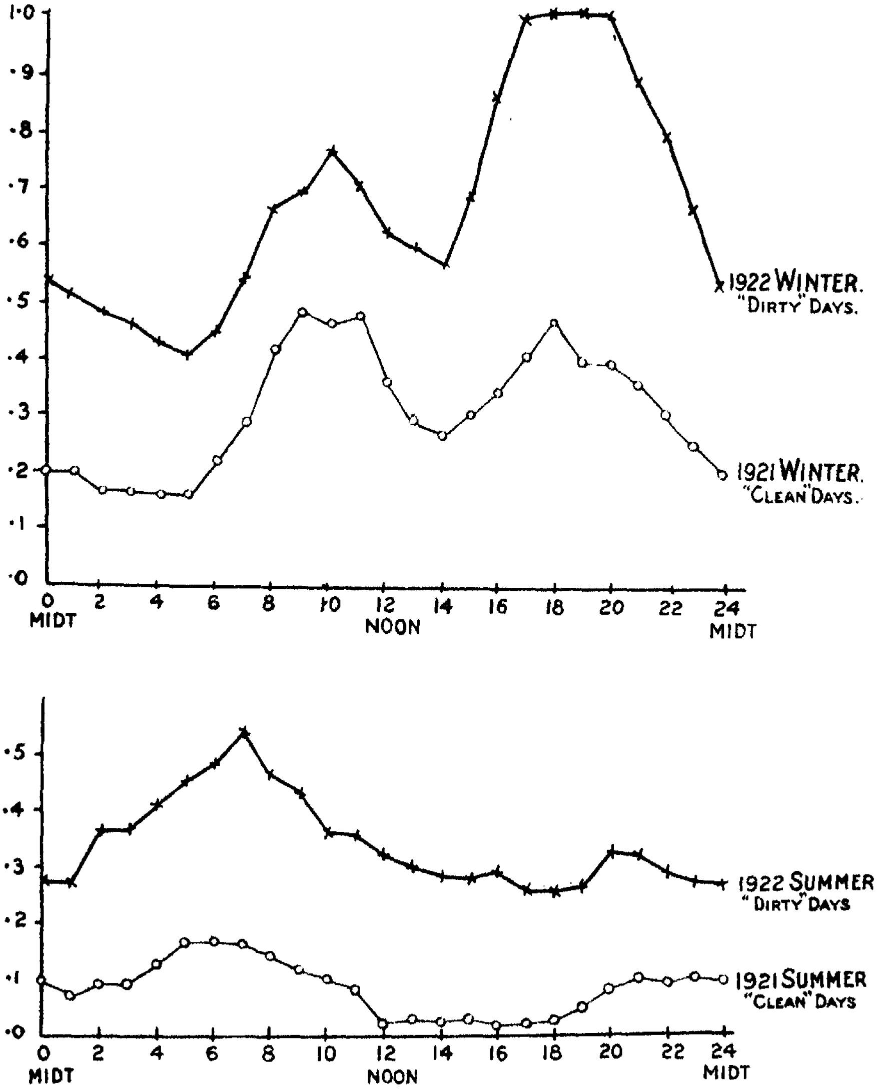

Fig. 2.—Pollution. Absolute hourly values (milligrammes per cubic metre).

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* In fig. 3, upper half, to save space, it has been raised to the 200 value.

The close approach of the pollution curve for summer, 1921, to the base line between 12 h. and 18 h. suggests that, even with a perfectly clear atmosphere, but little further reduction could occur in the ordinate of the corresponding portion of the potential gradient curve for summer, 1921. But the lowness of the afternoon pollution values in summer arises partly from insensitiveness in the apparatus. Thus, with a perfectly clear atmosphere a sensible approach to the base line may be expected even in the "clean" day summer potential gradient curve.

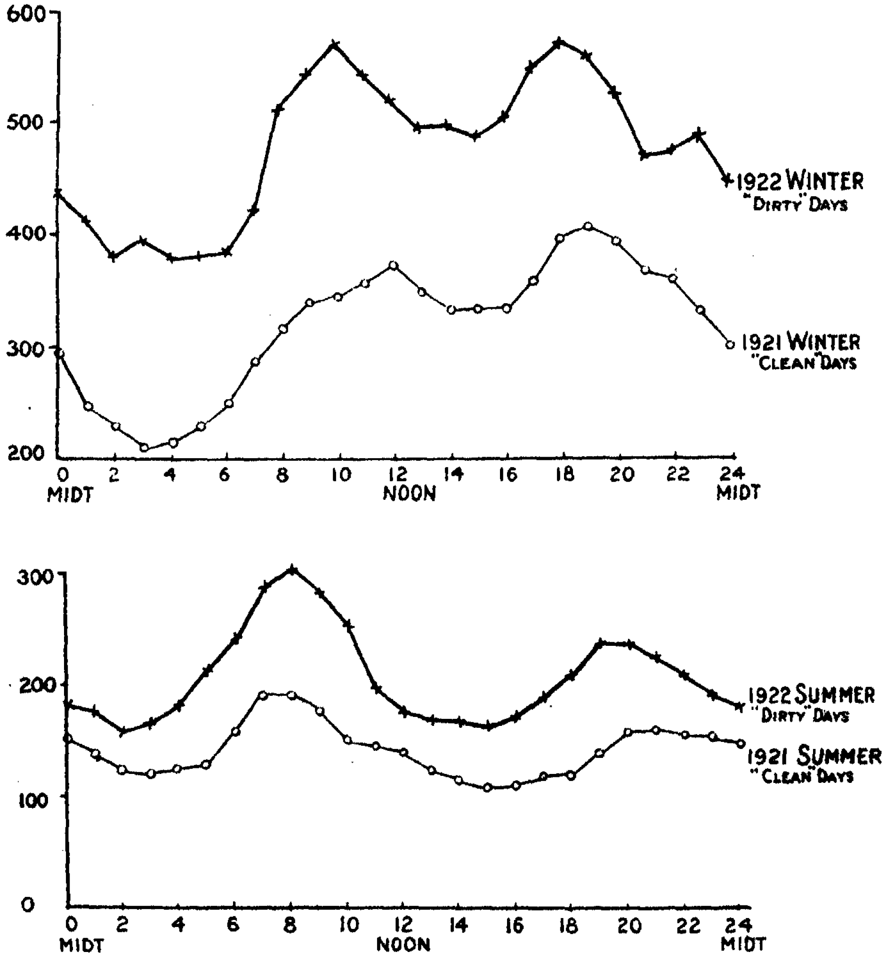

FIG. 3.—Potential. Absolute hourly values (volts per metre).

§ 10. The diurnal inequalities of pollution and potential gradient for the year and the two seasons, winter and summer, were analysed in Fourier series, and the amplitudes and phase angles are given in Tables X and XI. The phase angles refer to Greenwich mean-time. The Fourier series is supposed to take the form $c_1 \sin(t + \alpha_1) + c_2 \sin(2t + \alpha_2) + \ldots$, where t is time reckoned from Greenwich midnight and 15° is the angular equivalent of 1 hour in t.

Table X.—Pollution. Diurnal Variation. Values of Fourier Coefficients. (Unit 1×10^{-6} grammes per cubic metre.) (Time G.M.T.)

Season.	Days used.	c_1.	α_1.	c_2.	α_2.	c_3.	α_3.	c_4.	α_4.
			°		°		°		°
Year	" Clean "	32	251	72	196	18	44	10	321
Year	" Dirty "	43	202	108	197	21	15	14	270
Winter....	" Clean "	108	233	101	183	41	19	15	285
Winter....	" Dirty "	232	199	142	187	65	351	30	212
Summer	" Clean "	58	12	30	194	14	164	2	270
Summer	" Dirty "	65	353	36	234	17	163	7	326
Summer, 1921	" Clean "	56	22	29	216	15	177	5	214
Summer, 1922	" Dirty "	92	351	49	242	21	190	12	320

Table XI.—Potential Gradient. Diurnal Variation.

Values of Fourier Coefficients. (Time G.M.T.)

Season.	Days used.	c_1.	α_1.	c_2.	α_2.	c_3.	α_3.	c_4.	α_4.
		v/m	°	v/m	°	v/m	°	v/m	°
Year	" Clean "	33	211	46	186	3	78	5	325
Year	" Dirty "	48	215	50	191	14	36	4	276
Winter	" Clean "	69	209	46	171	9	353	1	147
Winter	" Dirty "	98	208	40	178	17	4	8	191
Summer	" Clean "	11	27	34	190	11	148	7	344
Summer	" Dirty "	19	290	50	200	13	93	8	338
Summer, 1921	" Clean "	13	8	28	183	8	128	6	5
Summer, 1921	" Dirty "	27	254	48	189	15	94	6	335
Summer, 1922	" Clean "	11	49	40	195	14	159	8	327
Summer, 1922	" Dirty "	21	334	53	209	5	93	10	340

In the case of pollution, Table X, the 24-hour term is larger than the 12-hour term in each of the two seasons, but the lesser variability of the 12-hour term phase angle leads to the 12-hour term being decidedly the principal term in the diurnal inequality for the whole year. The phase angle in the 24-hour term is invariably larger for the " clean " than for the " dirty " days. This implies a retardation of the maximum on the " dirty " days, the retardation being 3¼ hours in the case of the year, 2¼ hours in winter and 1¼ hours in summer.

The value 196° ascribed to α_2, in Table X, for the year in " clean " days implies that the earlier minimum of the 12-hour term in the case of pollution falls near $2\frac{1}{4}$ h. In the case of the year and winter the values of α_2 on " clean " and " dirty " days are nearly identical. But in summer α_2 increases substantially with the increase of pollution, *i.e.* pollution accelerates the hours of maximum and minimum in the 12-hour term.

There is obviously a considerable similarity between the phase angles in Tables X and XI, especially in the case of the 12-hour wave. The value of α_2 is always less for potential than for pollution, *i.e.* the maximum occurs later in the former element, but the difference is usually small. In both cases α_2 increases, *i.e.* the hour of maximum is accelerated, with increase of pollution. As against the intimate connection thus suggested, there is the fact that while c_2 in Table X shows a notable rise in the " dirty " days, especially in winter, there is no corresponding rise in c_2 in Table XI, except in summer. Thus there is no parallelism between the variations of the *amplitudes* of the 12-hour waves for pollution and potential.

In the case of the 24-hour wave, the difference between the corresponding phase angles for pollution and potential is greater. Also in the cases of the year and winter the value of α_1 for potential seems practically independent of the amount of pollution, whereas α_1 for pollution falls notably on the " dirty " days. On the other hand, the values of c_1 for potential agree with the corresponding values for pollution in showing a large rise as we pass from the clean to the dirty days. The same is true in general of c_3, though the summer of 1922 supplies an exception.

In the case of the 6-hour wave in potential, there is an apparent large difference of phase between summer and winter, to which there is no parallel in pollution. Also the value of c_4 for potential in summer seems unaffected by the amount of pollution. The value is, however, so small that accident may play the principal part in the result.

The 24- and 12-hour terms are the principal terms for both elements, but the variation in their relative values throughout the year is markedly different in the two cases, as the following values of c_2/c_1 show :—

—	Pollution. Values of c_2/c_1.			Potential. Values of c_2/c_1.		
	Year.	Winter.	Summer.	Year.	Winter.	Summer.
" Clean " days	2·24	0·94	0·51	1·36	0·67	3·01
" Dirty " days	2·53	0·61	0·55	1·04	0·41	2·67

The value of c_2/c_1 for pollution seems little influenced, except in winter, by the amount of pollution, and the difference between summer and winter, especially on " dirty " days, is comparatively small. In the case of potential, on the other hand, c_2/c_1 diminishes sensibly as pollution increases, and it is very much larger in summer, when pollution is low, than in winter when it is high. The natural inference is that pollution is in no way responsible for the high summer values of c_2/c_1 characteristic of potential gradient at Kew.

§ 11. Several attempts, not apparently very successful, were made to deduce diurnal inequalities of potential gradient for the ideal perfectly " clean " day. Table XII gives one set of results thus arrived at. They were derived by the assumption that pollution at any hour of any season increased the potential gradient at a uniform rate, 363 v/m being the equivalent of 1 milligram of dirt per cubic metre. This was the figure obtained from the " clean " and " dirty " day mean values of pollution and potential for the whole year when the potential figures were taken out—as they were in the original calculations—one figure beyond that shown here. A correction based on this figure and the mean hourly values of pollution for " clean " and " dirty " days combined was applied to mean hourly values of potential gradient for the " clean " and " dirty " days combined. Results are given for the year as a whole and the usual 4-month winter and summer seasons, the two years being combined. The inequality thus found for summer appears fairly probable, but the other two inequalities, especially that for winter, do not. As a matter of fact, when we take the values of potential gradient for corresponding hours of the representative " clean " and " dirty " days, and ascribe the difference to the corresponding difference of pollution, we get widely varying values for the potential equivalent of 1 milligram of dirt. The differences are not merely erratic from hour to hour, but tend to be much higher at one part of the day than another.

§ 12. A point to be borne in mind in this connection is that what the Owens' apparatus records is the atmospheric impurity a few feet above ground level. Assuming atmospheric pollution to influence potential gradient, it is practically certain that the influence will depend on the amount of pollution throughout a stratum of considerable height. On two different occasions, with the same pollution near the ground, there might be widely different pollutions even at 100 feet above ground level. Occasionally there is sunshine on the Observatory roof when fog is still thick at the level of the potential and pollution recorders, and thick fog may persist for hours in the low ground surrounding the Observatory when the sun is shining brightly in Richmond Park, less than two miles away.

A second point worthy of consideration is the possibility that the conditions

Table XII.—Diurnal Inequality of Potential Gradient,

Hour G.M.T.	1	2	3	4	5	6	7	8	9	10
Year	− 21	− 40	− 41	− 41	− 36	− 29	− 14	− 2	+ 9	+ 15
Winter	− 8	− 32	− 24	− 15	− 8	− 22	− 20	− 24	− 7	− 2
Summer	− 19	− 42	− 47	− 48	− 45	− 12	+ 18	+ 35	+ 32	+ 18

which favour the increase of pollution, *e.g.* a wind from the north-east, may also favour the increase of potential gradient. If this were the case, the rise of potential with increase of pollution might be due not to any direct influence of pollution, but simply to the presence of meteorological conditions which would lead to an enhanced potential even in the purest of atmospheres. That this cannot be a complete explanation seems pretty clear from the large differences observed between corresponding months of 1921 and 1922, but it is not at all unlikely that it is a partial explanation.

If we conclude, as the observed phenomena certainly suggest, that atmospheric pollution exerts a considerable influence on the phenomena of atmospheric electricity recorded at Kew, a doubt naturally arises as to the utility of the records. It may appear at first sight that a station suffering from air pollution is, so far as electrical observations are concerned, in a similar position to a magnetic observatory situated near an electric railway, and it may be thought that the proper course is to transfer electrical observations to an unpolluted neighbourhood. But it should be remembered that, at least in England, a polluted atmosphere is the rule, not the exception. It is doubtful whether there is any place in England where a pollution recorder would systematically fail to record sensible pollution. For a suburban station, Kew Observatory is in a comparatively clean neighbourhood. There is no building other than the Observatory itself producing smoke within a quarter of a mile of the instruments, and between the Observatory and London there is a large area practically uninhabited, including the Old Deer Park, Syon Park and the Royal Gardens. The prevailing winds are from the west or south-west, and London lies to the north-east. For information as to the conditions under which the major part of the population lives, Kew Observatory is much more representative than would be a station in a remote country district.

It has also to be remembered that, unless under very exceptional circumstances such as the prolonged coal strike in 1921, the state of the atmosphere as regards pollution will naturally not vary much from year to year, so that the value of the data for comparative purposes should not be much affected. On the other

1921 and 1922. Ideal "Clean" Day (volts per metre).

11	12	13	14	15	16	17	18	19	20	21	22	23	24	Mean.
+ 7	+ 19	+ 12	+ 17	+ 15	+ 14	+ 18	+ 20	+ **28**	+ 23	+ 15	+ 15	+ 3	− 4	156
− 5	+ 31	+ 27	+ **36**	+ 28	+ 7	+ 4	+ 8	+ 14	− 1	− 14	+ 5	+ 12	+ 10	200
− 1	0	− 8	− 7	− 16	− 3	+ 10	+ 16	+ 33	+ **35**	+ 28	+ 24	+ 7	− 7	107

hand, London continues to grow, and the population in the outer suburbs goes on increasing. Thus a tendency to increased pollution and a consequent secular rise in the potential gradient is to be expected, unless legislation against smoke production or improved methods of combustion intervene.

The conclusion that naturally suggests itself is that while it would be a mistake to discontinue atmospheric electricity observations at Kew Observatory, there would be advantages in having comparative records from some station having as pure an atmosphere as can be secured in the south of England. A good deal possibly might be learned from an intelligent comparison of corresponding Kew and Greenwich results. Both observatories lie to the south of the main London area, but one is in the west, the other in the east, so the wind directions associated with maximum pollution are presumably quite different for the two places. A comparison of the mean values of the potential gradient on days when the atmosphere is thick at the one station and comparatively clean at the other should be instructive.

On the Electrical Conductivity of Magnetite.

By Ernest Wilson and E. F. Herroun.

(Communicated by Prof. O. W. Richardson, F.R.S. Received January 18, 1924.)

The present paper deals with the Electrical Conductivity of certain varieties of Magnetite as affected by impressed voltage, temperature, compressive stress, and magnetisation. It is, of course, well known that the electric conductivity of metallic oxides is very sensitive to change in temperature,* and the change in dimension of magnetite itself due to magnetisation has also been studied.† In addition, the conductivity of minerals of various kinds, sometimes in the form of crystals, plays an important part in the problem of radio-telegraphy or telephony. It is felt that any addition to our knowledge of the subject of electric conduction in matter and its control is worthy of being recorded, and this is the object of the present communication. The varieties of magnetite chosen have widely different properties and compositions, and although much remains to be done, the present paper may prove of interest to those working at this important subject.

Description of the tested material.

New York State (exact locality not known). Density 4·86. This is a uniform hard and compact mineral with no indication of cleavage planes. Its fracture is bright and irregular with numerous glistening points and semi-metallic lustre. It is characterised by a high magnetic susceptibility which is highly affected by tensile and compressive stresses. The bar tested in the present experiments is the one originally used, and is referred to as the "original" specimen.

The variety referred to as New York (Slaty) is from the same district. Its density is 4.24 and it is less rich in magnetite than the original variety tested.

Arkansas. Density 4·70 to 4·82. This variety is remarkable on account of its high retentivity, and samples from this district are very uniform in their physical properties and are, as a rule, permanently magnetised when received. The material is hard and compact with irregular cleavage planes and almost vitreous fracture in some directions, whilst in others it exhibits a silky lustre. It has a much lower magnetic susceptibility than the original New York variety and requires much larger stress (compressive and tensile) to produce changes in its magnetic properties.[*]

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* Somerville, 'Sci. Abs.,' vol. 16, No. 116; Bidwell, 'Phys. Rev.,' Dec., 1917; Horton, 'Phil. Mag.,' 6s, vol. 11, 1906.

† K. Yamada, 'Tokyo Proc.,' October 7, 1913.

Russian (locality unknown). Density 4·72. This variety is compact with dull irregular fracture and many minute cleavages all in the same direction. It resembles the New York original variety in that its retentivity is small and its susceptibility is fairly high.

Tilly Foster. (New York State). Density 4·10 to 45·8. It is essentially an aggregate of magnetite, calcite and silicates, and has irregular glistening fracture in which the inclusions can be easily detected.

Instrumentation.

Throughout the work copper deposition has been resorted to in order to secure good electrical contact with the magnetite. The nature of the deposit obviously varied with the composition of the test-piece, and as the electrical resistance of the junction entered into the measurements it was most important to discover if any error was caused thereby. As an alternative to the method of including the junction in the test circuit, a potentiometer was employed to determine the fall of potential between two electrodes firmly pressed into contact with the test-piece. At the time of balance no current passed across the junction of the electrodes and the magnetite bar, and the variation in potential due to compressive stress or a magnetic field agreed with the variation in resistance as measured through the electro-deposited ends. The resistance box used had the advantage that proportional arms of 10,000 ohms and a variable resistance terminating in 10ths of ohms were provided. There was nothing special about the instruments, which were of standard type and calibrated. The lever arrangement and the provision for magnetising the test-piece when subjected to various compressive stresses were the same as used in previous work on magnetic susceptibility[†] and need not be described.

Specific Resistance and Temperature Co-efficient.

The specific resistances of all the varieties tested are given in ohms per cubic centimetre at the stated temperature in Table I. The voltage across the test piece at the time of balance is also given, as resistance is a function of the applied potential. On account of inclusions the dimensions of the specimen may play a part; for example, the Tilly Foster thin strip gave 15·1 as against 7·5 in the case of the short thick bar.

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[*] 'Phys. Soc. (London) Proc.,' vol. 31, Pt. 5, p. 299 (1919); 'Roy. Soc. Proc.,' A, vol. 101, p. 445 (1922); 'Roy. Soc. Proc.,' A, vol. 103, p. 185 (1923).

[†] 'Roy. Soc. Proc.,' A, vol. 101, p. 445 (1922); 'Roy. Soc. Proc.,' A, vol. 103, p. 185 (1923).

The temperature co-efficients are given between the limits of 10° C. and 100° C. before and after the heat treatment detailed in the paper.

It will be seen that in the case of Arkansas magnetite the co-efficient is practically unchanged after repeated heatings to high temperatures, while in other cases it is reduced to roughly half its initial value.

It should be mentioned that at atmospheric temperatures, say within the range of from 5° C. to 25° C., the co-efficient in the case of New York, Tilly Foster and Russian magnetites is very large, reaching, or even exceeding, the value of 0.012, but this rapidly diminishes with rise of temperature. A logarithmic formula was tried, but it was found that the exponential co-efficient was not really constant, diminishing as the temperature was raised.

Specimens in the original state were tested at the temperature of liquid air and the ratio of the resistance at that temperature to the resistance at 10° C. was as follows:—Russian 803, New York (Original) 972, New York (Slaty) 572, Arkansas 165, and Tilly Foster 651. It will be seen that the Arkansas differs from all the other varieties in that the ratio is very much smaller. The ratio in the case of the Russian bar was reduced to 298 after being heated to about 800° C.

Russian.

Experiments were made with a small cut bar of this magnetite and showed that its resistance varied from 683 to 598 ohms as the potential difference between its ends varied from 0·276 to 2·135 volts (*see* fig. 1). The temperature of the oil bath in which the specimen was placed varied from 18·8° C. to 19° C. during the experiment. The test was continued with another piece which had a resistance of 1,864 ohms at 27° C. when the applied voltage was 0·3. Voltages varying from 2 to 50 were then impressed upon the specimen and the resistance was permanently reduced to 620 ohms at 19·4° C. This change might possibly be attributed to the temperature which the specimen had under the temporary application of the larger voltages, but experiment shows that no permanent reduction in resistance is produced by the application of a temperature of about 150° C. With 50 volts applied for 10 seconds, the specimen being free in air, and the temperature sufficient to volatilise the paraffin oil on its surface, the resistance was 75 ohms, and it was 620 ohms on return to 19·4° C., which was the temperature of the oil bath. The same piece was then bombarded by an electric discharge from an induction coil and the resistance at 19° C. was finally 245 ohms.

The effect of temperature was further examined in the case of a round bar of this magnetite 3·1 cm. long and 1 cm. in diameter, which was placed vertically between plungers with a lever arrangement so that compressive stress could be applied if desired at any temperature. A platino-iridium junction was placed in contact with the bar, and a heating coil of platinum wire, covered with asbestos sheet, was wound on the specimen. The whole was then thickly lagged with asbestos. At each end of the test-piece copper strips served as electrodes for the measurement of resistance. Compressed asbestos board about 0·4 cm. in thickness was inserted at each end between the plungers and the copper electrodes to prevent the escape of heat in a longitudinal direction. The initial value of the resistance of the bar at atmospheric temperature was 73 ohms. The bar was slowly heated to 192° C. and allowed to cool, and the resistance returned to its initial value at room temperature. At 880° C. the resistance had the value 0·33 ohm, when the potential difference between the ends of the specimen was 0·002 volt. On cooling to atmospheric temperature the resistance had dropped to about one-seventh of the value it had in the first instance. Table II shows that subsequent heat tests to about 875° C. did not produce a further reduction in resistance at room temperature.

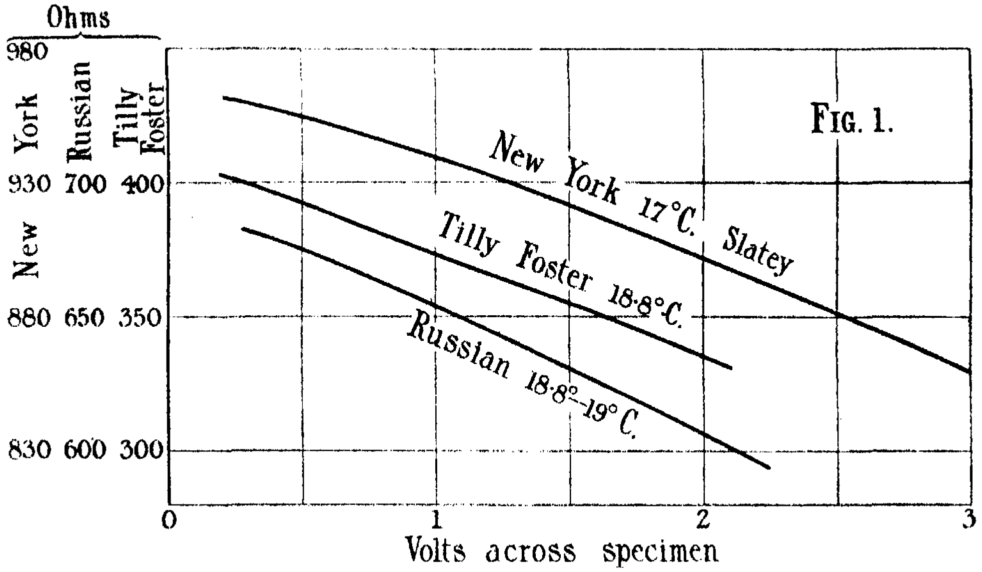


FIG. 1.

The first compression tests at atmospheric temperature were made with a cut bar, 3·9 cm. long and of square cross-section (1 cm. across each side), and the stress ranged from zero to about 900 kg. per square centimetre. Table III gives details of the experiments, and it will be observed that the longitudinal resistance varied from 0·45 to 0·63 per cent. on applying or removing the maximum stress; and this result is in close agreement with the percentage reduction obtained when the fall of potential between two copper wires pressed firmly on the surface of the bar was measured by the potentiometer method. In the case of the 3·1 cm. round bar above mentioned, the percentage diminution in resistance at room temperature, due to the application of 1,085 kg. per square centimetre, was 1·04 to 1·51 in the original state, and it was 1·7 after submitting the specimen to a temperature of 875° C. The variation in the transverse resistance at the centre of the bar, due to longitudinal compressive stress, is dealt with in the case of the other varieties, as the square bar unfortunately crushed when attempting the experiment. (*See* Table III.)

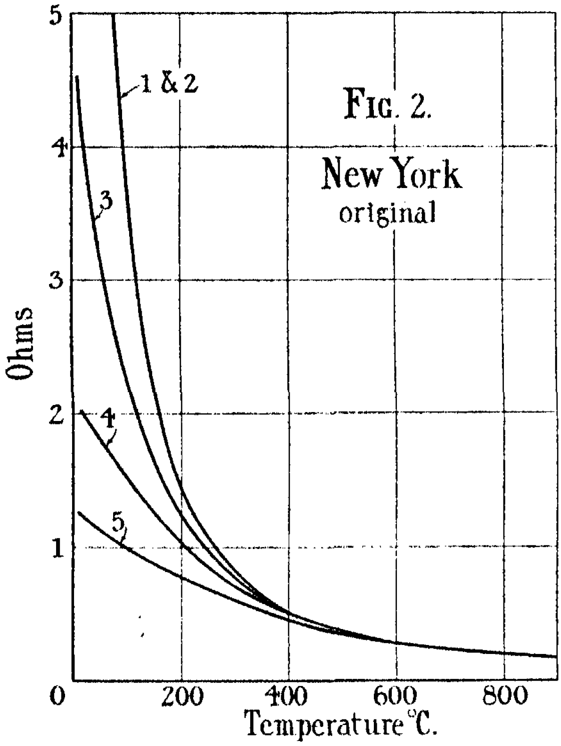
The specimen having a square section was subjected to a magnetic field by placing it in the gap of a ring-shaped stalloy yoke. It was thus magnetised longitudinally. The diminution of resistance between the ends of the bar due to the application of the magnetic force H = 1,520 was 0·44 per cent. when the test-piece was subjected to only a small compressive stress due to the weight of the lever (Table IV). The curve connecting variation in resistance with magnetic force resembles the ordinary curve of induction of ferro-magnetic matter. It was stated above that this specimen was unfortunately crushed when attempting the compressive stress tests.

New York State (*Original*).

The specimen tested had a length of 3.8 cm. and square cross-section (1 cm. across each side). Its specific resistance at 24° C. was found to be 1·49, which is less than the Russian variety (see Table I). It is interesting to note that the percentage diminution of longitudinal resistance at atmospheric temperature, due to the application of 887 kg. per square centimetre (see Table III), which amounted to 0·53 and 0·94, was almost identical with the diminution found by the fall of potential method when the electrical contacts were 3·4 cm. apart. It is noticeable that when the contacts were 0·9 cm. apart at the centre of the bar the percentage diminution had increased to 1·10. The change of transverse resistance at the centre of the bar was found to be 2·83 and 3·51 per cent. at maximum loading, and this is considerably greater than the variation in the longitudinal resistance.

This variety shows a continuous fall in its initial electrical resistance (7.69 ohms) at atmospheric temperature after heating to successively increasing temperatures (see Table II), and in this it resembles the Russian variety. It will be seen from the figures, and also from fig. 2, that after being raised to 920° C.

for the first time the resistance was 1·28 ohms at room temperature, and it dropped to 0·98 ohm after a second heating to the same temperature, and in each case the resistance at 920° C. was 0·154 ohms. The total change after the six successive tests amounts to a drop of 87·2 per cent., and it is possible that a further reduction would have been produced if the experiments had been prolonged. All the resistances were taken when the potential difference across the specimen was maintained constant at 0·05 volt. The effect of testing at constant current (0·05 ampere) is to slightly reduce resistance at the very high temperatures. The maximum drop in resistance due to the application of 887 kg. per square centimetre with 0·05 volt impressed upon the specimen was 10·8 per cent. when the temperature had the value 920° C., and it gradually diminished until the values given in Table III were obtained at room temperatures.



The magnetic susceptibility of this particular bar was obtained before and after the heating tests, and although its maximum value 1·46 is unaltered, it occurs at a force of 40 C.G.S. units as compared with 27 units in the first instance.

The variation of resistance between the ends of the bar when it was magnetised longitudinally is shown in fig. 3. Unstressed, the percentage diminution due to the application of a magnetic force H = 1,750 was 1·0, and owing to the reduction in susceptibility* it was reduced to 0·93 when the bar was in the same strength of magnetic field, but subjected to a longitudinal compressive stress of 887 kg. per square centimetre. The percentage diminution due to residual magnetism after the application of 1,750 C.G.S. units, was also smaller in the stressed condition. The curves in fig. 3 show how the transverse resistance varies when a magnetic field of given strength is applied in the stressed and unstressed conditions. When the magnetic force H = 1,520 is applied, the percentage drop in resistance (see Table IV) amounts to 1·55 with 16 kg. per square centimetre compressive force and 1·03 when the compressive force is 887 kg. per square centimetre, the magnetic field being the same in intensity.

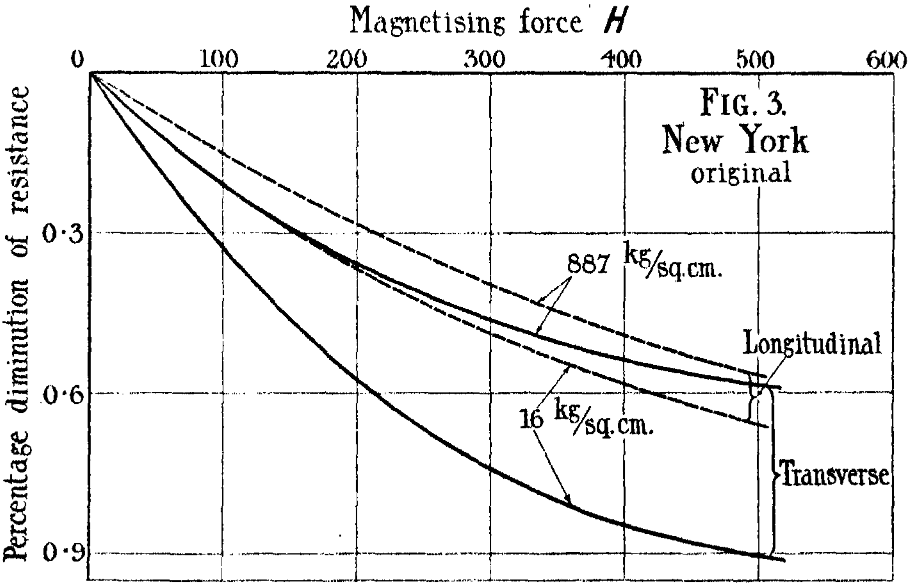


FIG. 3. New York original

When a strip of this magnetite was magnetised transversely in a field of 312 C.G.S. units, the longitudinal resistance was diminished 0·034 per cent., and it returned to its original value on removing the magnetic force.

New York State (*Slaty*).

This variety came from the same locality as the preceding; it differs in that it contains a considerable amount of slaty material, and this affects its physical properties. For example, its maximum magnetic susceptibility is 0·49 for a force of H = 50, as compared with 1·44 for a force of H = 27. The curve in fig. 1 shows the variation of resistance of a bar of this magnetite over a moderate range of voltage at constant temperature. It shows, as in the other cases, a fall in resistance with increasing voltage. After heating this specimen in an oil bath to a temperature of 168° C., the resistance was the same on return to room temperature. The specific resistance is high, as would be expected (Table I), and it reached the enormous value of 57,600 at the temperature of liquid air; but the temperature co-efficient is about the same as in the preceding variety.

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* *Loc. cit.*

A bar 3·9 cm. long and of rectangular section (1·04 square centimetre) was submitted to compressive stress of varying magnitude as in the previous examples; and it is noticeable that the variation in longitudinal resistance for a given stress is greater than in the denser mineral. The transverse resistance is also reduced by a greater though less marked percentage. It will be seen also that the percentage reduction in resistance, due to the application of a magnetic field, is more pronounced (Table IV). The following figures contrast the two varieties :—

Percentage Drop in Electrical Resistance.

	New York (Original).			New York (Slaty).		
H.	Unstressed.	887 Kg/cm.^{2}	Ratio.	Unstressed.	887 Kg/cm.^{2}	Ratio.
71	0·25	0·20	1·25	0·364	0·19	1·92
141	0·44	0·29	1·52	0·88	0·60	1·47
282	0·66	0·44	1·50	1·46	1·11	1·31
350	0·81	0·50	1·62	1·64	1·33	1·23
530	0·92	0·53	1·73	2·13	1·86	1·14
1520	1·55	1·03	1·50	3·3	2·9	1·14

Arkansas.

This variety of magnetite is remarkable on account of its high magnetic retentivity. Its specific resistance is the lowest of the magnetites tested, and it shows no diminution of resistance at atmospheric temperature over the range of voltage shown in fig. 1 (see Table I), nor after repeated heatings (see Table II); and in these respects it stands alone.

The longitudinal resistance in the case of a cut bar 3·8 cm. long and 1 cm. by 1 cm. cross-section was found to diminish 0·46 and 0·51 per cent. by the bridge method, and 0·45 and 0·47 per cent. by potentiometer, on the application of 887 kg. per square centimetre (Table III) at atmospheric temperature.

The cut bar 3·2 cm. long and 1 cm. by 1 cm. cross-section was prepared in the manner described and submitted to a series of heating tests. When the voltage between the ends of the bar was maintained constant at 0·041, the total drop in resistance between room temperature and 900° C. amounted to 88 per cent., and the drop was 92 per cent. when a constant current of 0·05 ampere was maintained throughout the test.

The effect of compressive stress upon resistance at 900° C. was tested, and a diminution in longitudinal resistance amounting to 2 per cent. was recorded on the application of 887 kg. per square centimetre.

It may be recalled that this variety of magnetite in comparison with others was least responsive to change in magnetic susceptibility either in tension or compression.

New York State (*Tilly Foster Mine*).

The specific resistance of this variety is of intermediate value, and, as shown in fig. 1, it is a function of the impressed voltage.

A bar 3·5 cm. long and 0·95 sq. cm. cross-sectional area was tested at atmospheric temperature for longitudinal and transverse resistance as affected by compressive stress (Table III). The longitudinal resistance as measured by the potentiometer method showed a very small change. On the other hand, the variation of transverse resistance at the centre of the bar was considerable. Unfortunately the specimen fractured when loading it during a heating test.

Table I.

	Specific Resistance—Ohms per c.cm.									Average Temperature Co-efficient between 10° C. and 100° C.	
	Temp. C.	Short thick bar.						Thin strip.		Before heating to maximum temp.	After heating to maximum temp.
		Volts.	Specific Res.	Volts.	Specific Res.	Volts.	Specific Res.	Temp. C.	Specific Res		
									0·2 Volt.		approx. 900° C.
New York (original)	19	0·14	1·98	0·0149	1·98	0·0015	1·98	— 16·5	— 1·93	0·0068 0·0079	0·0024
New York (Slaty)	17	1·8	71·8	0·97	74·8	0·177	76·9	—	—	0·0061	—
Russian	25	0·696	13·68	0·069	13·78	0·00107	13·82	— 16·3	— 110	0·0055 0·012	·0029 0·0061
Arkansas	7·0	1·75	0·59	0·133	0·60	0·014	0·601	— 14	— 0·74	0·0040 0·0027	0·0048 —
Tilly Foster	10	1·79	21·3	0·967	22·8	0·178	23·8	— 18	— 18·5	— 0·0079	—

Table II.—Electric Resistance at Atmospheric Temperature after successive heat tests.

		1	2	3	4	5	6	7	8	9
Arkansas	Temp. C. Ohms.	Atmos. 1·1	112 0·99	188 1·00	460 1·04	725 1·2	1,025 1·42	350 1·36	355 1·29	900 1·32
New York (original)	Temp. C. Ohms.	Atmos. 7·69	220 7·14	520 3·57	660 2·04	920 1·28	915 0·98	— —	— —	— —
Russian	Temp. C. Ohms.	Atmos. 72·9	192 72·9	880 10·2	900 12·0	875 11·35	865 11·6	875 11·8	— —	— —

Table III.—Drop in Resistance due to the Application of 887 kg./cm.^{2} Compressive Stress.

Variety.	Dimensions.				Temp. C.	Drop in Electrical Resistance.					Remarks.
	Length.	Thickness and Breadth.		Area.		Potentiometer Method.				Bridge Method.	
						Distance between contacts.	Per cent.	Distance between contacts.	Per cent.	Per cent.	
New York (original)	3·8	1·0	1·0	1·0	23·9	cm. 0·90	1·1 1·1	cm. 3·4	0·52 0·70	0·53 0·94	Longitudinal.
					19·5	1·0	2·83 3·51	— —	— —	— —	Transverse.
New York (Slaty)	3·9	0·95	1·1	1·04	20·5	—	—	3·1	2·64 1·24	— —	Longitudinal.
					15·5	1·0	3·95 3·95	— —	— —	— —	Transverse.
Russian	3·9	1·05	0·95	0·998	19·9	—	—	2·4	0·40 0·61	0·45 0·63	Longitudinal.
Arkansas	3·8	1·0	1·0	1·0	17·7	1·0	1·9 1·72	— —	— —	0·46 0·51	Longitudinal.
					19·3	—	—	3·2	0·45 0·47	— —	Longitudinal.
Tilly Foster	3·5	0·95	1·0	0·95	19·4	—	—	2·8	0·15 0·07	— —	Longitudinal.
					18·0	1·0	2·25	—	—	—	Transverse.

Table IV.—Drop in Resistance due to the Application of Magnetic Force.

Variety.	Dimensions.				Temp. C.	Magnetic Force H.	Drop in Resistance per cent.	Compressive stress kg./cm.^{2}	Remarks.
	Length.	Thickness and Breadth.		Area.					
New York (original)	3·8	1·0	1·0	1·0	20·5	1,750	1·0	16	Longitudinal.
					20·5	1,750	0·93	887	Longitudinal.
					19·6	1,520	1·55 0·298*	16	Transverse.
					19·9	1,520	1·03 0·11*	887	Transverse.
New York (Slaty)	3·9	0·95	1·1	1·04	16·2	1,520	3·3 0·53*	16	Transverse.
					16·7	1,520	2·9 0·26*	887	Transverse.
Russian	3·9	1·05	0·95	0·998	24·0	1,520	0·44	16	Longitudinal.

* Due to residual magnetism.

The Difference-Periodogram—A Method for the Rapid Determination of Short Periodicities.

By C. E. P. Brooks, M.Sc.

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I.—*The Basis of the Method.*

1. The examination of a long series of observations in the search for periodicities by harmonic analysis is a tedious process. The method outlined below, although rough, has the merit of being much more rapid in its application, and has been found useful in the preliminary exploration of long meteorological records of periodic or quasi-periodic components. It is also useful in the study of periodicities of intermittent recurrence or variable length.

The basis of the method is the division of a series of observations into sections which are nearly, but not quite, equal to half the length of the suspected periodicity. If each section were exactly half the periodicity the first, third, fifth, etc., sections would all occur in the same position relatively to the periodic curve, while the second, fourth, sixth, etc., would occur a half-cycle away. If each section is slightly *less* than half the length of the periodicity, then the third section will fall at a slightly earlier phase than the first, the fifth earlier than the third and so on, until after a certain interval the nth section occurs at a similar phase to the first. The number of sections required to bring this about depends on the relation between their length and the length of the periodicity. If the sections selected had been slightly *longer* than half the periodicity, the phase would advance somewhat between the first and third sections, and so on until the cycle was repeated. Thus by plotting the mean values of all the odd sections and drawing a curve through them we could obtain an idea of the length of the underlying periodicity. The even sections could be plotted in the same way, and if the series of observations were completely represented by the periodic function under investigation, these two curves would be the reverse of each other. Thus by substituting for the mean value of each section its difference from the mean of the whole series, and reversing the sign of all the even sections, we can bring the latter into line with the odd sections and draw a single curve representing all the observations.

There is, however, the possibility that the observations are not completely represented by a single periodic function; for instance, they may result from the combination of the one we are investigating with one having a much longer period. Near a maximum of this longer periodicity, both odd and even sections will have a high value, and if we reverse the signs of the even sections, instead of having a smooth curve we shall have a zig-zag. We can smooth out this zig-zag by taking the mean of successive values, *i.e.*, we take the second section, reverse its sign, add it to the first section, and divide by two. This is merely equivalent to subtracting the second section from the first, the second from the third, the fourth from the third, the fourth from the fifth, and so on, dividing by two in each case. Obviously the division merely alters the scale of the curve without affecting the relation of its parts, and this step can be omitted.

This process of smoothing by taking successive differences works well enough when we are near a crest or trough of the longer periodicity, but it leads to difficulties if we are on one of the slopes, or if we have to deal with a secular variation. Suppose the whole series of observations has an upward trend, so that we have the following series :—

$$-6 \quad -4 \quad -2 \quad 0 \quad 2 \quad 4 \quad 6$$

Forming the differences in the manner set out above, we have :—

$$-6-(-4), \quad -2-(-4), \quad -2-0, \quad 2-0, \quad 2-4, \quad 6-4$$

or—

$$-2 \qquad +2 \qquad -2 \qquad +2 \qquad -2 \qquad +2$$

Thus we again have a zig-zag oscillation, and in order to eliminate this, we must again smooth by adding successive numbers and dividing by two. The result would be the same if we took the mean of four, six, or any *even* number of successive figures (*see* §5).

Thus in order to bring out the influence of the particular periodicity under investigation in a series of observations, and to eliminate the effects of longer periodicities or of a secular variation, we perform the following operations :—

(1) Divide the series into a number of equal sections, a, b, c, d, e, etc., each slightly greater or slightly less than half the length of the periodicity.

(2) Obtain the mean values of each of these sections.

(3) Form the differences $(a-b)$, $-(b-c)$, $(c-d)$, $-(d-e)$, etc.

(4) Form the means of successive differences, so that we have :

$$\tfrac{1}{2}\{(a-b)-(b-c)\}, \quad \tfrac{1}{2}\{-(b-c)+(c-d)\}, \quad \tfrac{1}{2}\{(c-d)-(d-e)\}, \text{ etc.}$$

(5) Plot the figures obtained in (4) with a horizontal time scale.

These operations are represented graphically in fig. 1. The curve A represents a harmonic oscillation combined with a small secular variation. This curve has been divided into equal sections whose mean values are represented by the continuous horizontal lines B_1, B_2, B_3 . . . The signs of the even terms B_2, B_4, . . . are reversed, and the broken horizontal lines B'_2, B'_4 . . . .

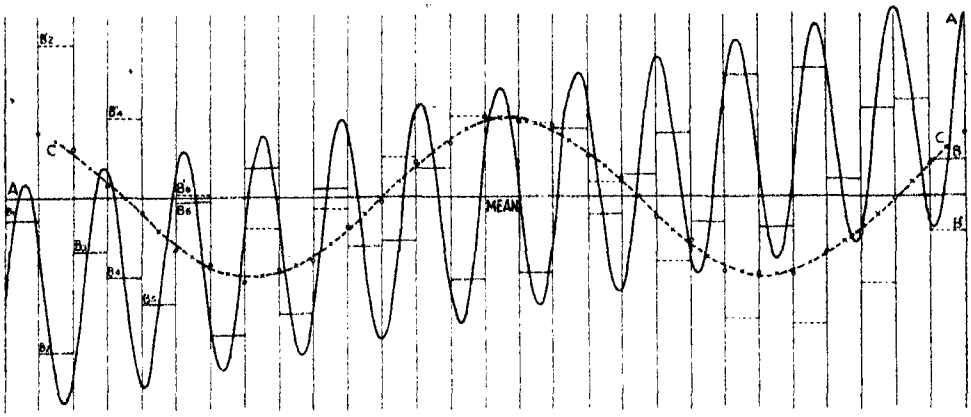

Fig. 1. Illustration of the construction of a Difference Curve

represent these negative values of B_2, B_4 . . . Next the small circles represent the mean values $\frac{1}{2}(B_1 + B'_2)$, $\frac{1}{2}(B'_2 + B_3)$, etc.—the division by two being retained for clearness in the diagram. Finally the crosses represent the means between successive circles, and the broken curve C drawn through them is the "difference-curve" required.

The periodicity in the original observations under investigation is represented in the curve so obtained by another periodic function of different length, amplitude and phase, and we have now to find out the relation between them.

2. Let the periodic function which is to be investigated be given by the equation—

$$F(t) = B \sin\left(\frac{2\pi t}{P} + \phi\right) \tag{1}$$

where P is the period, ϕ the initial phase at $t = 0$, and B the amplitude. The data from which the computation is to start incorporate the mean values of F (t) for intervals of length U. Since the mean value corresponds with the middle of an interval we may appropriately use the notation :—

$$S_{n-\frac{1}{2}} = \frac{1}{U}\int_{(n-1)U}^{nU} F(t)\,dt = \frac{BP}{\pi U} \sin \frac{\pi U}{P} \sin\left[\frac{2\pi}{P}(n-\tfrac{1}{2})\,U + \phi\right] \tag{2}$$

The difference between consecutive values of $S_{n-\frac{1}{2}}$ is T_n where—

$$T_n = S_{n-\frac{1}{2}} - S_{n+\frac{1}{2}} = -\,2\,\frac{BP}{\pi U} \sin^2 \frac{\pi U}{P} \cos\left[\frac{2\pi}{P}\,nU + \phi\right]. \tag{3}$$

Reversing the sign of alternate differences we have terms V_n such that—

$$V_n = (-1)^{n-1}\,T_n = \frac{2BP}{\pi U}\sin^2\frac{\pi U}{P}\cos\left[\frac{2\pi}{P}\,nU + \phi - n\pi\right] \tag{4}$$

If we smooth by taking the mean of consecutive values of V we have

$$W_{n+\frac{1}{2}} = \tfrac{1}{2}\,(V_n + V_{n+1}) = \frac{2BP}{\pi U}\sin^3\frac{\pi U}{P}\cos\ \left[(n+\tfrac{1}{2})\left(\frac{2\pi U}{P} - \pi\right) + \phi\right]. \tag{5}$$

These values of W are plotted on a time scale and a curve (the "difference-curve") is drawn through them, and we can identify a harmonic variation with period C and the first maximum at $t = T_0$, say—

$$W = A\cos\frac{2\pi\,(t - T_0)}{C}. \tag{6}$$

If this is in step with the term $W_{n+\frac{1}{2}}$ when $t = (n+\frac{1}{2})\,U$, then assuming that $C > 2U$ and $P > U$, either

$$\frac{1}{P} - \frac{1}{2U} = \frac{1}{C}; \qquad P = \frac{2CU}{2U + C}; \qquad \phi = 2\pi - \frac{2\pi T_0}{C} \tag{7A}$$

or else

$$\frac{1}{P} - \frac{1}{2U} = -\frac{1}{C}; \qquad P = \frac{2CU}{C - 2U}; \qquad \phi = \frac{2\pi T_0}{C} \tag{7B}$$

and in either case

$$A = \frac{2BP}{\pi U}\sin^3\frac{\pi U}{P} \tag{8}$$

and

$$B = \frac{A}{2}\left(\pi\frac{U}{P}\right)\frac{1}{\sin^3 \pi U/P}. \tag{9}$$

It will be seen later that it is desirable to have C large compared with U. To do this we must make P nearly equal to 2U. If $P = 2U$ C becomes infinite and the method breaks down. The most convenient relation to adopt is one which makes C equal to about half the length of the series available.

In equation (7) we have hitherto assumed that P is greater than U, but this assumption is not included in equation (5). We must accordingly examine the cases where P is less than U. The general form for equation (5) is—

$$W_{n+\frac{1}{2}} = \pm\frac{2BP}{\pi U}\sin^3\frac{\pi U}{P}\cos\left[(n+\tfrac{1}{2})\,(2\frac{\pi U}{P} - 2\,m\pi) + \phi\right], \tag{10}$$

where the value of the term within the brackets has been changed by $-(2n + 1)\,m\pi$, m being a positive or negative integer. This change makes no difference to the numerical value of the expression, but reverses the sign when m is odd. Then we have the following values of (7)—

$$m = 0, \qquad P = \frac{2UC}{C \pm 2U} \text{ as before}$$

$$m = 1, \qquad P = \frac{2UC}{3C \pm 2U}$$

$$m = 2, \qquad P = \frac{2UC}{5C \pm 2U},$$

and so on. In the two latter cases P is less than U, and by equation (8) the value of A will be much less than that of B. The variation of A/B with increasing values of U/P is shown in fig. 2, from which we see that for all values of $U/P > 1$ the ratio A/B is less than 0·5. Hence, unless B is very large, in which case the periodicity would easily be recognised in the original observations without the necessity for analysis, a period less than U would fail to give any appreciable amplitude in the difference-curve. Accordingly if we first eliminate any periodicities of great amplitude (such as the daily or annual

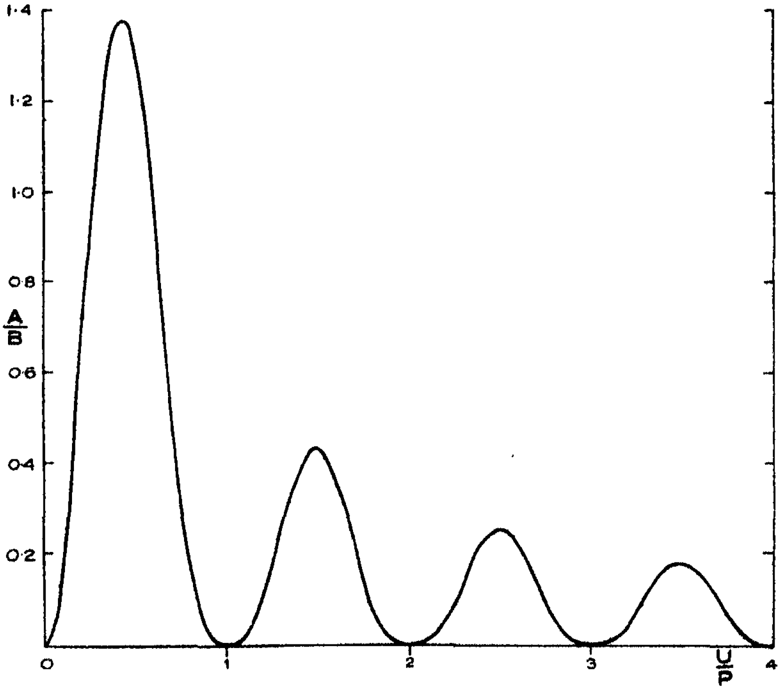

FIG. 2.—Curve showing variations of A/B with increasing values of U/P.

variation) shown by the observations, this possibility need not be taken into account.

If P is large compared with 2U, the value of the term $\sin^3 \pi U/P$ rapidly becomes inappreciable, and A again becomes very much less than B. Hence the effect of plotting the difference-curve is practically to destroy all periodicities in the original set of observations, except those in the neighbourhood of 2U, enabling the latter to be separated out. Any secular variation is completely eliminated. In order to distinguish between the two alternatives given by (7A) and (7B), it is merely necessary to take two values of U differing by a small amount.

Values of $2UC/(C \pm 2U)$ when $U = 1$ are given in Table I of the Appendix.

3. The effect of a small error or uncertainty in the estimation of C becomes less important as C increases in value, both absolutely and relatively to C. With $C = (10 \pm 1)$ U, we have for the higher alternative value of P limits of 2·57U and 2·44U, and for the lower alternative value limits of 1·64U and 1·69U. In general, if C is 10U or more, a small error e in the value of C causes an error of approximately $4eU^2/C^2$ in the value of P.

4. We have found in equation (8) an expression for the amplitude B of the original periodicity in terms of the amplitude A of the difference-curve. If the difference-curve shows clear and regular fluctuations, A can be read off without difficulty. If the difference-curve is too irregular for this, the first term of the harmonic series can be calculated trigonometrically from the working figures in the usual way, but a shorter method often gives sufficiently accurate results. In an ordinary periodic function the curve is usually complicated by harmonics of the second and higher orders, but in the difference-curve a second harmonic will only rarely be present, because the values of P and P′ necessary to give C and C/2 are not commensurable. Hence the amplitude A can be found by dividing the difference-curve into sections of length C/2 centred about the maxima and minima respectively, and integrating (from the working sheets) over these sections. If ΣM and Σm are the summations of the maximum and minimum sections respectively, the amplitude A is $1{\cdot}57\,(\Sigma M - \Sigma m)/n$. An example is given in §8.

Values of $B/A = \frac{1}{2}(\pi U/P)\ 1/\sin^3 \pi \dfrac{U}{P}$ for different values of U/P are given in Table II of the Appendix.

5. If the series under investigation results from the superposition of a number of periodic functions of different length, the difference-curve may show two or more periodicities of different length, so that the fluctuations due to the shorter interfere with the precise determination of the length, amplitude and phase of

the longer. A similar result may be due to short-period irregular fluctuations. These short-period fluctuations can be eliminated to some extent by smoothing. Thus in No. (4) of the operations summarised on p. 347, in place of forming the means of successive pairs of differences, we can form the means of four. Then we can write equation (5)—

$$W_{n+\frac{1}{2}} = \tfrac{1}{4}(V_{n-1} + V_n + V_{n+1} + V_{n+2})$$
$$= \frac{2BP}{\pi U} \sin^3 \frac{\pi U}{P} \cos\left[(n + \tfrac{1}{2})\left(\frac{2\pi U}{P} - \pi\right) + \phi\right] \cos\left(\frac{2\pi U}{P} - \pi\right). \quad (11)$$

For values of P for which C is large, *i.e.*, P nearly equal to 2U, the additional term $\cos(2\pi U/P - \pi)$ is nearly unity, but for values of P for which C is small, *i.e.*, P nearly equal to U, it approaches zero. Hence the effect is to reduce the amplitude of the short-period fluctuations of the difference-curve, while leaving the long-period fluctuations almost unaltered. In general, smoothing over 2 m, where m is any integer, has the effect of multiplying the right-hand term in equation (5) by $\cos\frac{m}{2}(2\pi U/P - \pi)$, and this term has to be taken into account in calculating the amplitude. The phase is not affected. It is necessary to smooth over an even number of terms of V in order to eliminate any secular variation or periodicity much longer than that under investigation; smoothing over an odd number of terms does not effect this completely. Obviously 2 m should not be greater than C/2.

II.—*Examples of the Application of the Method.*

6. In applying the method of the difference-periodogram in practice we have to consider two main cases; in the first case, we suspect the existence of a periodicity between definite narrow limits, while in the second case we are searching for all the periodicities that exist without any idea as to what we expect to find. In the first case, let us call the limiting values x and y, where $y - x$ is small. Then we can take as our value of U either the nearest convenient period shorter than $\frac{1}{2}x$ or the nearest convenient period longer then $\frac{1}{2}y$. If we adopt $U = \frac{1}{2}x$ and the real period is y, we have—

$$P = y = Cx/(x + C), \text{ whence } C = xy/(y - x).$$

This is the lowest value of C which we expect, and in order to bring out its existence by eliminating shorter fluctuations in the manner described in §5, we can smooth the differences over the nearest even number of terms less than half this value.

As an example we may take the monthly amounts of rainfall in London over

100 years, published by the Meteorological Office in diagram form (*). This diagram when studied from a distance, so that the lines separating the individual years cannot be distinguished, gives no obvious indication of a twelve-monthly periodicity, and for the purpose of the argument we may suppose that, instead of knowing that such a periodicity exists, we merely suspect the existence of a periodicity somewhere between 11 and 13 months. Then we can put $U = 5$ or 7 months, and we find that according to the method set out above,

$$\text{(i) } U = 5,\ x = 10,\ y = P = 13,\ C = 8\cdot7U;$$
$$\text{(ii) } U = 7,\ y = 14,\ x = P = 11,\ C = 7\cdot3U.$$

Thus in the first case we can smooth the differences over four, in the second case over two only.

Table I.—Tabulation of rainfall observations.

No.	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)
1	8·72		—	14·69		—
		−3·88			+1·75	
2	12·60		—	12·94		+ 1·93
		−4·27			+0·18	
3	8·33		−8·05	13·12		− 2·47
		−1·40			−2·65	
4	9·73		−2·43	15·77		− 5·76
		+1·50			−3·11	
5	11·23		+1·43	12·66		− 6·17
		+1·74			−3·06	
6	9·49		+1·54	15·72		+ 1·82
		−0·41			+4·88	
7	9·08		+3·62	20·60		+12·10
		−1·29			+7·28	
8	10·37		+2·64	13·32		+ 9·68
		+3·58			+2·40	
9	13·95		−0·39	15·72		+ 5·91
		+0·76			+3·51	
10	13·19		+0·71	12·21		+ 6·70
		−3·44			+3·19	
11	9·75		+1·24	15·40		+ 4·07

Table I illustrates the method. In column (*a*) the total rainfall is given for the first to fifth, sixth to tenth months, and so on. In column (*b*) the differences between these totals are given, in the form (1)−(2), −[(2)−(3)], (3)−(4), etc. In column (*c*) the differences in column (*b*) are combined in overlapping sums of four. Columns (*d*) and (*e*) repeat the procedure of columns (*a*) and (*b*), but employing a unit of seven months instead of five, and in (*f*) the differences of column (*e*) are combined in pairs. Only the first few lines of the calculation are shown, but in fig. 3 the whole set of figures from column (*c*) are plotted. This curve shows a well-marked periodicity with a length equal to about 12U, the maxima falling at the following five-monthly points :—

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* London Meteorological Office, 'One Hundred Years of Rainfall for London,' (Diagram).

13 31 44 56 67 77 90 104 114 126 137 150 164 176
187 199 208 (222) 234

giving 1 interval of 9U, 2 of 10U, 2 of 11U, 5 of 12U, 4 of 13U, 3 of 14U, and 1 of 18U. The latter, which is the first of the series, is evidently abnormal; if we commence with the second maximum, at 31U, we have 17 cycles with an average length C = 11·94U, corresponding with a periodicity of either 12·01 or 8·54 months. On plotting the figures in column (*f*) we find that the former value is correct, *i.e.*, the periodicity is 12·0 months, but in the first few years this periodicity did not appear.

The amplitude cannot be taken directly from fig. 3 with much accuracy, the curve being too irregular. From the working sheets, the amplitude of the difference cycle reduced to a unit of one month is found by the short method of §4 to be 1·57 × 0·32 = 0·50 inches, corresponding with an amplitude in the original periodicity of about 0·37 inch. (By Appendix Table II.)

Starting with 31U, the comparison between the dates of the actual maxima and those recurring at intervals of 12U is as follows :—

Observed Maxima.	U (31 + 12*n*).	Difference.
31	31	0
44	43	+1
56	55	+1
67	67	0
77	79	−2
90	91	−1
104	103	+1
114	115	−1
126	127	−1
137	139	−2
150	151	−1
164	163	+1
176	175	+1
187	187	0
199	199	0
208	211	−3
(222)	223	−1
234	235	−1

The mean of the figures in the difference-column is —0·44, indicating that the epochs of the maxima are 7·44U, 19·44U, 31·44U, etc. Hence the

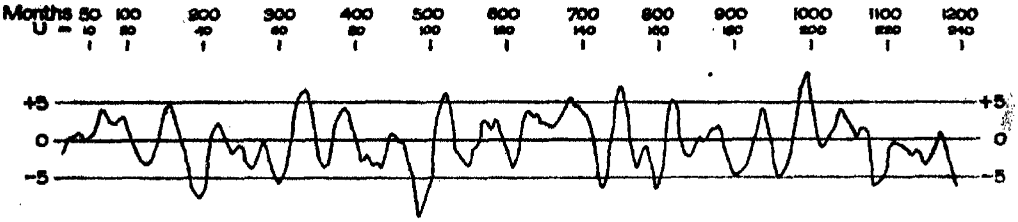

FIG. 3.—Difference periodogram, London rainfall.

phase of the 12-months periodicity at $t = 0$ is $2\pi \times 7 \cdot 44/12 = 223°$ (by 7B), giving for the first harmonic in the annual variation of London rainfall:

$$F(t) = 0 \cdot 37 \sin(t + 223°).$$

The annual variation calculated by harmonic analysis from the monthly means for the whole period is :—

$$F(t) = 0 \cdot 44 \sin(t + 226°).$$

The agreement is sufficiently good to show that fairly reliable results may be obtained from the difference-periodogram even for amplitude and phase. Fig. 3 also shows that the annual variation has been well-developed in certain series of years and poorly-developed in others, for instance in the last few years, after about 210 U (= 88th year or 1901) the annual variation has been almost non-existent. Many similar facts can be deduced from the difference-curve which throws light on the changes which any periodicity undergoes from time to time.

7. In the second case we have a series of observations which we wish to examine for periodicities, but with no preconceived ideas as to what we expect to find. In this case we adopt successive values of U, starting with the smallest convenient value, and continuing through larger and larger values. It is necessary that any periodicity which may exist should appear on at least two of the difference-curves, in order that we may discriminate between the alternative values, and on one of these curves the corresponding value of C should not be much less than 10U. Now C = 10U corresponds with periodicities of 1·67U or 2·50U, and the criterion for determining what successive values of U we shall adopt is that each pair of successive values shall be in the ratio of 1 : 1·5. If we are dealing with a series of monthly values, we have on the left of Table II the values of U which satisfy this condition, and on the right the nearest values which it will usually be convenient to adopt.

Table II.—Successive values of U to be adopted.

$U_{n+1} = 3/2U_n$.	Adopted Values.	$U_{n+1} = 3/2U_n$.	Adopted Values.
Month.	Month.	Year.	Year.
1	1	1·42	1·25 1·5
1·5	2	2·14	2
2·25	3	3·20	3
3·37	4	4·81	5
5·06	5	7·21	7
7·59	6 8	10·81	10
11·39	12	16·22	15

In order to find the highest value of U, say U_m, which it is permissible to adopt with a series of n observations we put $U_m = n/22$, this value of U_m will give two complete oscillations in the difference-curve (smoothed over two) when $C = 10$.

8. As a practical example of this method, the monthly means of Greenwich temperatures from 1841 to 1905 were analysed. These figures have been exhaustively examined by the full method of harmonic analysis by D. Brunt,* whose results thus constitute a check on the efficiency of the difference-periodogram. There is a large annual variation, which was eliminated by subtracting from each monthly figure the corresponding monthly average for the whole period. There are 780 monthly values and $n/22$ is approximately 36, so that we can work with all the values of U given in Table II up to three years. The working occupied about a week and is too long to reproduce here, but the periodograms with U = 12 months and U = 1·25 year are reproduced in fig. 4. In this figure the upper full curve results from putting U = 12 months,

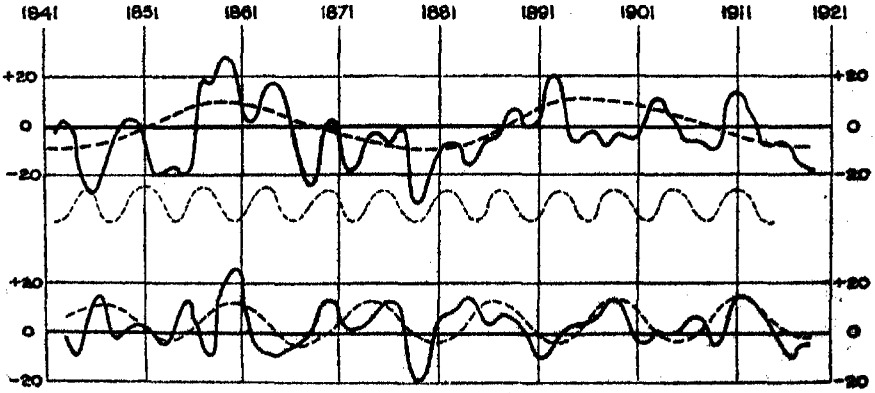

Fig. 4.—Difference periodogram, Greenwich temperature.

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* London, 'Q. J. R. Meteor. Soc.,' vol. 45, p. 323 (1919).

and appears to be made up of two principal components, which are indicated by broken lines; of these the longer has a value of $C = (38 \pm 5)U$, while the shorter has a mean value of approximately $C = 6{\cdot}1U$. The lower curve shows indications of a periodicity with $C' = 10U'$ (broken curve), but this is not very well developed owing to the interference of a shorter periodicity which cannot be exactly defined. These values of C correspond to the following periodicities:

$C = 33\text{–}43U \qquad P = 1{\cdot}89\text{–}1{\cdot}91$ years or $2{\cdot}13\text{–}2{\cdot}10$ years.
$C = 6{\cdot}1U \qquad P = 3{\cdot}0$ years or $1{\cdot}5$ years.
$C' = 10U' \qquad P' = 1{\cdot}67 \times 1{\cdot}25 = 2{\cdot}08$ years or $2{\cdot}50 \times 1{\cdot}25 = 3{\cdot}13$ years.

It appears at first sight that either of the alternative values of P' could be used, and reference to difference-curves drawn for other values of U was necessary in order to show that the real period is about 2·1 years.

A rough approximation to the amplitude of the 2·1 year periodicity can be obtained from fig. 4. The range of the broken curve is approximately 2·0° F, whence $A = 1{\cdot}0°$ F and $B = \frac{A}{2}\left(\pi\frac{U}{P}\right)\frac{1}{\sin^3 \pi U/P} = 0{\cdot}76°$ F. (by Table II of Appendix). The difference-curve is, however too irregular for an accurate measure of the amplitude by this means, and it would be better to use the method of § 4. Taking the first maximum as occurring in 1859 and using a value of 40 for C, we find from the original table of differences:—

Period.	Sum.	Years.	Mean.
−(1842–1848)	+ 7·2	7	+1·03
+(1849–1868)	+ 1·7	20	+ ·09
−(1869–1888)	+18·6	20	+0·93
+(1889–1908)	+ 0·7	20	+0·03
−(1909–1919)	+ 6·0	11	+0·54
Total	+34·2	78	+0·44

From this the amplitude A is 0·70° F. and B = 0·52° F., and the value of A = 1·0° F. was an over-estimate.

Since the length of the periodicity is more than 2U, in calculating the phase we have to use (7B) whence—

$\phi = 2\pi\, T_0/C$, or putting $T_0 = 1859 = 18{\cdot}5$, and $C = 38$,
$\phi = 18{\cdot}5/38 \times 2\pi = 175°$.

The periodicity nearest to 2·11 years found by Brunt in the Greenwich temperatures from 1841 to 1890 was one of 812 days or 2·22 years. The amplitude is 0·62° F. and the phase at 1841·0 is 247°. At first sight the difference between 2·22 and 2·11 years is not important, but with U=1 year a periodicity of 2·22 years gives a value of C equal to 20. On reference to fig. 4 (upper curve) we see that the first maximum cannot be placed later than 1861 and the second cannot be placed earlier than 1892, so that the lowest possible value of C is 31 years and the longest period of about 2 years which can be deduced from this curve is 2·14 years.

Now on page 332 of his paper Brunt gives a more detailed discussion of the periods near 24 months and 26 months, in which he shows that from 1841 to 1884 the predominant period was 23·6 months and from 1885 to 1905 the predominant period was 27·9 months. The weighted mean of these two, 25·0 months or 2·08 years, comes very close to our value of 2·1. There is another point. In the upper curve of fig. 4 the area of the curve below the horizontal axis is much greater than the area above. This indicates the presence of a period of approximately 2·0 years (1·97—2·03 years). This may quite well be Brunt's 23·6 month (1·97 year) period.

9. In other cases only the lengths of the periodicities were calculated, for comparison with Brunt's periodicities. The comparative list is as follows—

Difference-Periodogram.		Brunt.
(*a*) From 1841 to 1876	1·74 months	
1876 to 1884	1·57 ,,	Too short for Brunt's net.
1884 to 1895	1·74 ,,	
1895 to 1905	1·61 ,,	
(*b*) 4·4 months		4·34 months.
(*c*) Not found		5·00 and 5·06 months.
(*d*) 5·7 months (not well developed)		—
(*e*) 7·3 months (not well developed)		7·5 months.
(*f*) 18–19 months, probably nearer 19		19·5 months.
(*g*) Not found		22·7 months.
(*h*) 25·3 months or 2·1 years, already referred to, but found on several other curves.		26·6 months. Well developed.
(*i*) 47·7 months		47·9 months.
(*k*) 62 months		61 months.

10. The results of the above comparison are distinctly encouraging, as most of Brunt's shorter periodicities are approximately represented. Within certain limits the difference-periodogram seems likely to be of considerable value. The amount of labour is comparatively small, and the results generally leap quickly to the eye. On the other hand, it must be admitted that the results, especially as regards amplitude and phase, are not of such a high order of accuracy as those obtained by the use of harmonic analysis. Further, since the resolving power of the difference-periodogram is limited, it is not well adapted

for analysing closely a series which is composed of a large number of periodicities of small amplitudes and of the same order of length. It is to be regarded as analogous to the low-power object-glass of a microscope, which gives a rapid survey of the specimen under examination. By this means areas of special interest can be selected, which can then be examined by the high-power of the microscope—in this case harmonic analysis.

Mr. F. J. W. Whipple has taken great interest in the difference-periodogram and has contributed very materially to the theory of the method as set out above, and I wish to take this opportunity of acknowledging his assistance.

APPENDIX.

Table I.—Values of $2C/(C \pm 2)$ when $U = 1$.

C	2C/(C+2).	2C/(C−2).	C.	2C/(C+2).	2C/(C−2).
3	1·20	6·00	17	1·789	2·267
4	1·33	4·00	18	1·800	2·250
5	1·43	3·33	19	1·810	2·235
6	1·50	3·00	20	1·818	2·222
7	1·56	2·80	21	1·826	2·211
8	1·60	2·67	22	1·833	2·200
9	1·64	2·57	23	1·840	2·190
10	1·667	2·50	24	1·846	2·182
11	1·692	2·44	25	1·852	2·174
12	1·714	2·40	26	1·857	2·167
13	1·733	2·364	27	1·862	2·160
14	1·750	2·333	28	1·867	2·154
15	1·765	2·308	29	1·871	2·148
16	1·778	2·286	30	1·875	2·143

Table II.—Values of $\frac{B}{A} = \frac{1}{2}\left(\pi\frac{U}{P}\right)\frac{1}{\sin^3 \pi U/P}$.

U/P	0·00	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08	0·09
0·2	1·55	1·45	1·35	1·26	1·19	1·12	1·06	1·01	0·97	0·93
0·3	0·90	0·87	0·85	0·82	0·80	0·78	0·77	0·76	0·75	0·74
0·4	0·73	0·73	0·73	0·73	0·73	0·73	0·74	0·75	0·76	0·77
0·5	0·78	0·80	0·82	0·84	0·87	0·90	0·93	0·96	1·00	1·05
0·6	1·10	1·15	1·20	1·27	1·35	1·45	1·55	1·65	1·75	1·90
0·7	2·05	2·3	2·4	2·6	3·0	3·3	3·7	4·1	4·6	5·3
0·8	6·2	7·0	8·0	9·3	11·6	14·5	17·9	22·0	26·3	36·0

Particles of Long Range from Polonium.

By L. F. BATES, B.Sc., Trinity College, Cambridge, and J. S. ROGERS, B.A., M.Sc., Trinity College, 1851 Research Student of the University of Melbourne.

(Communicated by Prof. Sir E. Rutherford, F.R.S. Received Feb. 14, 1924.)

(From the Cavendish Laboratory, Cambridge.)

I.—*Introduction and Method of Investigation.*

With the discovery of new groups of α-rays of long range from radium C and thorium C*, the question of the emission of small groups of long-range particles from all radioactive substances, which emit α-rays, naturally presented itself. Polonium, which emits a group of α-rays of range 3·93 cm. in air at 15° C. and a pressure of 760 mm. of mercury, was at once considered a substance that might be investigated with advantage.

The method of investigation was that previously employed in the examination of the α-rays from the above sources. A source was placed at a known distance from a zinc sulphide screen and the numbers of scintillations were observed, by means of a specially designed microscope with a large field of view and of high light-collecting power, when mica sheets of different stopping powers were placed between the source and screen. The source was screwed into the end of a horizontal brass rod, which was attached to the carrier of a reading microscope, so that it could be adjusted in definite positions. By plotting the observed numbers of scintillations (corrected, of course, for any contamination or natural effect of the screen) against the equivalent air gap between the source and screen, the ranges of any long-range particles, if present in sufficient number, could be found.

2.—*Preparation of Polonium Sources.*

Two sources of polonium (denoted below by A and B), which had been prepared by Dr. J. Chadwick, were first used. Both were obtained from a solution of radium D, which was separated in 1919 by Sir E. Rutherford and Dr. Chadwick from a parent solution of a large quantity of radium chloride. This solution was freed from lead by precipitation, and since then has been continuously used in the Cavendish Laboratory as a source of polonium. The deposits were prepared by continuously rotating copper discs for some time in the warm solution. It was quite probable that these sources would be contaminated with minute traces of radium which were present in the radium D solution. In fact, it was established later that such contamination did occur.

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* Bates and Rogers, 'Roy. Soc. Proc.,' A, vol. 105, p. 97 (1924).

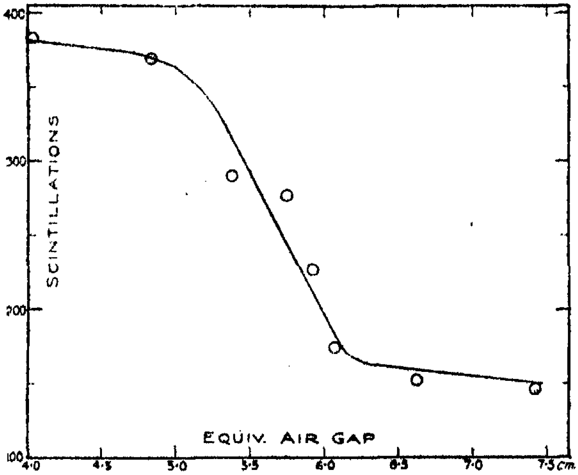
Preliminary experiments with these sources showed the presence of a group of particles whose range was about 6·7 cm., and another group whose range was approximately 9·9 cm. Now radium C emits particles of ranges 6·97 cm. and 9·3 cm., and although it seemed most unlikely that an error in range of as much as 6 mm. could possibly be made with the experimental arrangements described, yet it was necessary to show that these newly observed groups of particles were not due to minute traces of radium C which was formed by the disintegration of the radium contamination mentioned above. It is known that for every 10^7 α-rays of range 6·97 cm. emitted by radium C, 380 particles of range 9·3 cm. are also emitted. However, from the curves obtained, it was obvious that if the particles of range 6·7 cm. were due to radium C, the 9·9 cm. particles certainly were not, for their number was some hundreds of times greater than would have been found if they arose from radium C. In fact, with the small number of 6·7 cm. particles observed, it would have been impossible to detect any 9·3 cm. particles. Accordingly, it was decided that the particles of range 9·9 cm. were emitted by polonium.

It was consequently only necessary to trace the origin of the 6·7 cm. particles. To test for the presence of radium, the two sources A and B were in turn placed in a closed tube which could be connected to an evacuated emanation electroscope. After each source had remained in the tube for many hours, air, together with any emanation present, was admitted into the electroscope. The collapse of the electroscope leaf in both cases showed that both sources liberated emanation.

In order to establish the presence of any particles of range between 4 and 7 cm., it was therefore necessary to obtain a source of polonium in such a manner that no radium could possibly be present. A polonium source, C, was then prepared from the contents of a number of old emanation tubes, kindly provided by Sir E. Rutherford for this purpose. These were carefully washed many times in caustic soda, nitric acid and distilled water, to remove traces of organic matter adhering to the outside of the tubes. Each tube was then carefully examined for the presence of mercury used in filling the tubes with emanation, and any tube containing visible traces was rejected. The satisfactory tubes, about eighty in number, were broken, finely crushed and treated with a 20 per cent. solution of hydrochloric acid. The resulting solution was reduced to a convenient volume by evaporation and the polonium source was obtained by exposing the lower surface of a copper disc, which was elsewhere completely covered with shellac, in the hot solution for about an hour and a half, the disc being continually rotated during the exposure. A few small silvery patches on the source showed that all the selected emanation tubes had not been entirely free from mercury.

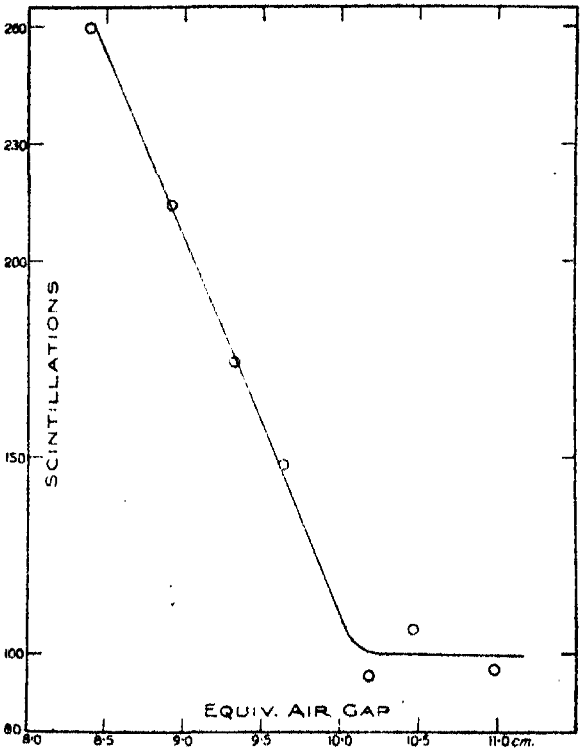
3.—*Ranges of New Groups of Particles.*

(*a*) *Particles of Range* 6·1 *cm.*—With source C, a new group of particles, whose range from five determinations was 6·1 ± 0·1 cm., was found. A typical determination is shown in Curve I, where the source was 2·44 cm. from the screen and the range found was 6·2 cm. The mica sheets used in these experiments varied in stopping power from 1·45 to 5·49 cm. of air and they were all calibrated in position using a source of thorium B + C. These particles were not noted in the preliminary experiments owing to the presence of radium C on sources A and B, in quantities sufficient to mask them.



Curve I.—Polonium—particles of range 6·1 cm.

(*b*) *Particles of Range* 10·0 *cm.*—Since the presence of radium C in small amounts would not influence the determination of the range of the second group of particles, experiments were carried out with all three polonium sources. In order to provide the necessary stopping powers, subsidiary pieces of mica were placed in position before the mica sheets used in the last experiments. As these pieces of mica had been calibrated in definite positions with respect to a zinc sulphide screen, the experimental values of their stopping powers were corrected from the results of Marsden and Richardson, as described in an earlier paper.* A typical result is given in Curve II, obtained by placing source C 1·43 cm. from the screen and using a subsidiary piece of mica of stopping power equivalent to 3·87 cm. of air. The range found from this curve was 10·1 cm. Three determinations were made with source A, two with B and one with C; the mean value of the range was 10·0 ± 0·1 cm.



Curve II.—Polonium—particles of range 10·0 cm.

(*c*) *Particles of Range* 13·1 *cm.*—Investigation of the remaining particles of still longer range showed that one further group of definite range was present. As in the last section, subsidiary pieces of mica were used to provide the necessary stopping powers. The numbers of particles were small and their range could not be determined with the same accuracy as in the foregoing experiments. A typical result is shown in Curve III, where the source C was placed 1·00 cm. from the screen and the stopping power of the subsidiary piece of mica was 7·75 cm. of air; the range found from this curve was 13·1 cm. Two determinations were made with source A, two with C and one with B, the mean range being 13·1 ± 0·2 cm.

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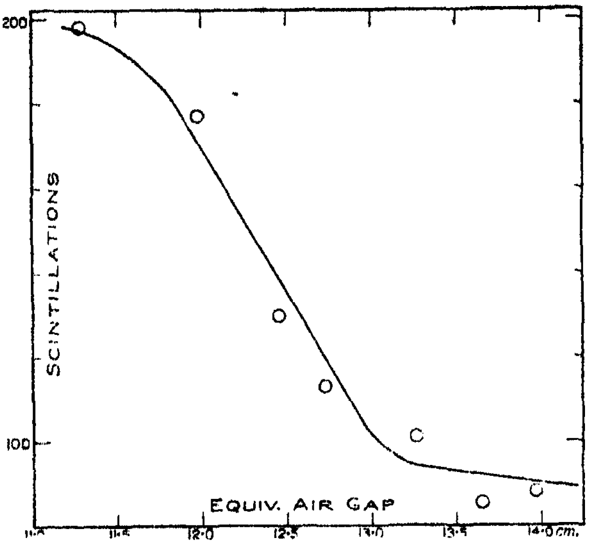
* Bates and Rogers, *loc. cit.*



Curve III.—Polonium—particles of range 13·1 cm.

(*d*) *Particles of Range greater than* 13·1 *cm.*—The particles of long range were investigated with stopping powers up to 13·5 cm., but beyond this range they were not further examined, as their numbers were very small and there was no evidence to suggest that they were other than long-range H-particles excited by the passage of the 3·93 cm. α-rays through matter. From the brightness of their scintillations alone, it is considered that the particles of ranges 6·1, 10·0 and 13·1 cm. are α-rays.

4.—*Relative Numbers of the Long-Range Particles.*

It was known from the above experiments that the number of the long-range particles compared with that of the α-rays of range 3·93 cm. was very small. To determine the relative numbers the source C was mounted about 1·5 cm. from the screen, and the number of 3·93 cm. α-rays producing scintillations per minute was found by the rotating wheel and slit method,* and the number of 6·1 cm. particles was found by taking the difference in the numbers of scintillations observed with stopping powers of 4·6 and 6·3 cm. of air approximately between the source and screen. The relative number of the 6·1 particles with respect to the 3·93 cm. α-rays was so small that difficulty was experienced in finding the ratio. If the distance of the source from the screen was such that the numbers of 6·1 cm. particles were sufficiently large for accurate counting, then the numbers of 3·93 cm. α-rays reached the upper limit for counting, even when the finest slit, 0·069 mm. wide, was used on the wheel, whose effective diameter was 11·8 cm. As the numbers of 10·0 and 13·1 cm. particles were still smaller, it was necessary first to determine the number of the 6·1 cm. particles with respect to the 3·93 cm. α-rays and later to find the numbers of 10·0 and 13·1 cm. particles relative to those of range 6·1 cm.

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* Chadwick, 'Phil. Mag.,' vol. 40, p. 739 (1920).

Table I.—Numbers of Particles of Ranges 6·1 and 3·93 cm.

Stopping Power, 1·5 cm.	Stopping Power, 4·6 cm.	Stopping Power, 6·3 cm.	Percentage.
2935	281	97	0·00116
4045	319	113	0·00095
3195	245	77	0·00097
7800	606	211	0·00094
5814	538	238	0·00096
		Mean Percentage : 0·00098.	

In Table I are given five determinations with source C. The first three were made as described above ; the first column gives the numbers of scintillations observed with the rotating wheel and slit for a given number of counts, usually sixteen, each of one minute duration. The second and third columns give the numbers of scintillations, for an equal number of counts, with the stopping powers of approximately 4·6 and 6·3 cm. of air respectively. All counts were corrected for contamination effects. The fourth column gives the percentage of the particles of range 6·1 cm. with respect to the α-rays of range 3·93 cm.

The last two determinations of Table I were made by placing the source nearer the zinc sulphide screen, so that much larger numbers of the 6·1 cm. particles produced scintillations. In order to reduce the number of 3·93 cm. α-rays sufficiently for accurate counting, when the same rotating wheel and slit was used, the wheel was rotated more rapidly and a screen was placed at intervals in front of the source, so that the latter was able to send α-rays through the slit approximately only once in every six revolutions of the wheel. This virtually increased the effective diameter of the wheel by a corresponding factor. By observation of the number of scintillations for a given number of "open" transits of the slit, and from a knowledge of the total number of transits made per minute, the total number of α-rays able to produce scintillations, if the slit had been "open" a whole minute, could be calculated. The number of transits made per minute was observed several times during an experiment, and the mean frequency of the wheel was thus obtained. Any error due to irregularity in the speed of rotation was more than compensated by the gain in accuracy in the determination of the number of 6·1 cm. particles. The numbers given in rows four and five of the first column are the calculated numbers of scintillations which would have been produced in sixteen minutes with the wheel and slit in the absence of the screen. The values of the percentage agree with those of the preceding determinations. The very good agreement of the last four percentages in Table I is considered somewhat beyond the degree of accuracy attainable with the method; the first result, which is higher than the others, has been given only half weight in calculating the mean percentage, but no reason for its exclusion can be found.

To determine the numbers of particles of ranges 10·0 and 13·1 cm. with respect to those of range 6·1 cm., the source was fixed about 1·3 cm. from the zinc sulphide screen, and the numbers of scintillations for a given number of counts, each of one minute duration, were found when suitable mica sheets were inserted between the source and screen to provide stopping powers approximately equal to 4·1, 7·9, 10·7 and 13·6 cm. of air respectively. The difference between the numbers observed with the first two stopping powers gave the number of 6·1 cm. particles; the differences between the numbers with the second and third and between those with the third and fourth stopping powers gave respectively the numbers of 10·0 and 13·1 cm. particles. The results of five determinations are summarised in Table II.

Table II.—Numbers of Particles of different Ranges emitted by Polonium. (Source C.)

Range 6·1 cm.	Range 10·0 cm.	Range 13·1 cm.	Range greater than 13·2 cm.
644	329	164	48
547	311	160	38
563	316	137	52
431	216	117	31
445	201	123	30
Totals 2630	1373	701	199

Now, from Table I, it follows that with every 10^7 α-rays of range 3·93 cm. from polonium, the source emits in addition 98 particles of range 6·1 cm., and moreover, from Table II, for every 98 such particles there are also emitted 51 and 26 particles of ranges 10·0 and 13·1 cm. respectively, together with about seven particles of longer range.

All the experiments just described were carried out with source C, because of the radium contamination on sources A and B, which made it impossible to determine the numbers of 6·1 cm. particles. However, this contamination could not affect the determination of the relative number of the 10·0 and 13·1 cm. particles, and Table III shows the results obtained for sixteen counts, each of one minute duration, with the sources A and B and the appropriate stopping powers.

Table III.—Relative Numbers of Particles of Ranges 10·0 and 13·1 cm.

	Range 10·0 cm.	Range 13·1 cm.	Range greater than 13·2 cm.
Source A	654	318	98
Source B	594	340	95
Totals	1248	658	193

From Table III it follows that, if the number of 10·0 cm. particles from the sources is taken to be 51, then the number of 13·1 cm. particles is 27, thus showing that the relative numbers of 10·0 and 13·1 cm. particles are the same with sources A and B as with source C.

5.—*Discussion.*

It has been already stated that when the brightness of the scintillations produced by the 6·1, 10·0 and 13·1 cm. particles is considered with regard to the residual ranges of the particles, they all appear to be α-rays. For a similar reason, the particles of range exceeding 13·2 cm. are considered to be long-range H-particles.

It is important to establish from what radioactive substance the newly discovered particles arise. In the first place, as the particles are emitted from a source prepared from the contents of old emanation tubes, they must originate from a decay product of the emanation. Secondly, as the particles are present on sources deposited on copper discs in a radium D solution, they must be emitted by a product of radium D, *i.e.*, either by polonium or by a substance chemically similar to it. If, however, the substance producing these particles is a long-lived product similar to polonium, one would expect that the numbers of the long-range particles relative to the 3·93 cm. α-rays from polonium would depend on the age of the source used, instead of being directly proportional to the number of these α-rays. Unfortunately, it was impossible, on account of the radium contamination on sources A and B, to decide this point in the case of the 6·1 cm. particles, and although an attempt was made in the case of the 10·0 cm. particles, their numbers were so small that the experiment was impossible with our experimental arrangements. However, it is of interest that the relative numbers of the 10·0 cm. particles with respect to the 13·1 cm. particles, determined with all three sources, A, B and C, agree so closely, for these sources were prepared in the months of June, February and December, 1923, respectively, and further, A and B were obtained from a parent solution, quite different from the parent solution for source C. This agreement indicates that these two groups of particles arise from the same substance, if short-lived products of polonium are excluded. The formation of short-lived branch products of polonium might be represented in the usual schematic manner,* involving the emission of β-rays, but as a β-ray emission from polonium has not been recorded, this mode of disintegration cannot at present be supported; although it must be pointed out that such β-radiation would be very weak and perhaps beyond the range of observation of previous experiments.

Finally, therefore, since no β-ray evidence of branch products has been noted, and as no evidence of long-lived products similar to polonium has been obtained, it seems most reasonable to consider that the long-range particles described in this paper are emitted by polonium itself.

It is interesting to compare the relative numbers of the new long-range particles from radium C, thorium C and polonium. This has been done in Table IV.

In this table, for each substance, the number of α-rays of the range which preponderates is taken as 10^6. It will be seen that thorium C gives rise to the greatest numbers of long-range particles, there being approximately six times as many as in the case of radium C, while the numbers for polonium are slightly less than one-third of those of radium C. Further, although the numbers in the above table can be regarded as approximate only, when the method by which they were obtained is taken into consideration, it is still interesting to note that the numbers in the groups of long-range particles from any one substance appear to be in quite simple ratios, *e.g.*, for radium C this ratio for the successive numbers of particles is 6 : 2 : 1, for thorium C, 4 : 1 : 1, and for polonium, 4 : 2 : 1.

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* *Vide* Marsden and Perkins, 'Phil. Mag.,' vol. 27, p. 690 (1914).

Table IV.—Ranges and Relative Numbers of the long-range Particles from Radium C, Thorium C and Polonium.

Radium C.	Range cm.	3·8*	7·0	9·3	11·2	13·3
	No.	300	10^6	38	12·5	6·4
Thorium C.	Range cm.	4·8	8·6	11·5	15·0	18·4
	No.	$5·4 \times 10^5$	10^6	220	47	55
Polonium	Range cm.		3·9	6·1	10·0	13·1
	No.		10^6	9·8	5·1	2·6

* The presence of this group of α-rays has been deduced by K. Fajans ('Phys. Zeit.,' vol. 12, p. 369, 378, 1911, and 13, p. 699, 1912), from the experiments of Hahn and Meitner ('Phys. Zeit.,' vol. 10, p. 697, 1909) on recoil products from radium C, and he has estimated their range and relative number from the rate of decay of the recoil products. So far, owing to experimental difficulties, this group of α-rays has not been isolated.

6.—*Summary.*

Polonium has been examined by the scintillation method for the emission of long-range particles, and it has been found that for every 10^7 α-rays of range 3·93 cm. emitted, there are also present 98, 51 and 26 particles of ranges 6·1 ± 0·1, 10·0 ± 0·1 and 13·1 ± 0·2 cm. respectively, together with about 7 particles of longer range, which are probably H-particles. It is considered, from the relative brightness of the scintillations alone, that these particles are α-rays. Also from the evidence available it is deduced that these particles are emitted by polonium itself.

In conclusion, we wish to express our thanks to Sir E. Rutherford for his continued interest and encouragement throughout the research.

The Refractive Indices of Calcite and Aragonite.

By W. L. Bragg, F.R.S., Langworthy Professor of Physics, Manchester University.

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1. The two crystalline forms of calcium carbonate, calcite and aragonite, have been analyzed by X-ray methods, and they both display strong double refraction. It is therefore of interest to see whether the large difference in the refractive indices for light polarized in different planes can be explained by the atomic arrangements in the crystals.

The electron theory of dielectric media supposes that the atoms of the medium become polarized under the influence of an external electric field. The positive and negative components of the atom suffer a relative displacement, which is equivalent to the development of an electric doublet placed at or near the centre of the atom. The moment of the doublet is proportional to the strength of the electric field in its immediate neighbourhood, the constant of proportionality being characteristic of the atom considered. The local field which causes the polarization of the atom may for convenience be divided into two parts, the first being the force arising from charges in the field, including the doublets of the polarized medium not in the immediate neighbourhood of the atom, the second being the force arising from the doublets in its immediate neighbourhood. In isotropic media, such as liquids or amorphous solids, the average effect of the neighbouring doublets will be the same whatever the direction of the electric field which causes polarization. In crystals of lower symmetry than that of the cubic system, this will not be the case. The influence of the neighbouring doublets on an atom will depend on the orientation of the electric field with reference to the crystal axes; this will be the case both for the alternating fields of a wave train as well as for a steady field. The effective dielectric constant will therefore depend upon the direction of the electric vector of the waves, and since the velocity of light is inversely proportional to the square root of the dielectric constant, the crystal will display double refraction.

2. Calcite is optically uniaxial, owing to its possessing an axis of trigonal symmetry. Aragonite, which has orthorhombic symmetry, is biaxial, but two of the principal refractive indices are very nearly equal, so that the angle between the optic axes is small ($2V = 18°\ 10'$ for the D line). Both crystals

have strong negative birefringence. In the course of correspondence about the structure of aragonite, Mr. T. V. Barker pointed out to the author the striking relationship between the refractive indices of the two crystals. These indices have the following values for the sodium D line :—

Calcite .... $\varepsilon = 1 \cdot 486$ (Electric vector parallel to trigonal axis).
$\omega = 1 \cdot 658$ (Electric vector perpendicular to trigonal axis).
Aragonite .... $\alpha = 1 \cdot 530$ (Electric vector parallel to c axis).
$\beta = 1 \cdot 681$ (Electric vector parallel to a axis).
$\gamma = 1 \cdot 686$ (Electric vector parallel to b axis).
Acute bisectrix...c axis. Optic axial plane (100).

The density of calcite is 2·75 and that of aragonite 2·94. Allowing for this difference in density, it will be seen that ε for calcite corresponds to α for aragonite, and that ω for calcite corresponds to β and γ for aragonite. The small difference between β and γ is in accord with the form of the aragonite crystal, in which the "c" axis is an axis of pseudo-hexagonal symmetry. Aragonite simulates a uniaxial crystal for which $\varepsilon = 1 \cdot 530$, $\omega = 1 \cdot 683$.

A comparison of the crystal structures as analyzed by X-rays suggests a reason for this relationship. The arrangement of the atoms in planes perpendicular to the trigonal axis of calcite is very similar to that of atoms in planes perpendicular to the pseudo-hexagonal axis of aragonite. In both cases the planes are alternately composed of Ca ions and CO_3 groups, arranged at the corners of a triangular net work which has almost identical dimensions in calcite and aragonite. The CO_3 groups are built up in both cases of three oxygen atoms arranged symmetrically around a central carbon atom, and lie parallel to the planes. The oxygen atoms are closely packed around the carbon atom, a distance of about 1·30 Å separating the oxygen and carbon centres. The indices ω, β and γ correspond to an electric vector parallel to the planes whereas ε and α correspond to an electric vector perpendicular to the planes. The refractive indices show that the polarization for a given field is much greater when the field is parallel to the CO_3 groups than when it is perpendicular to them.

3. Accepted values for the refractivities of the calcium carbon and oxygen atoms in these crystals show that more than 80 per cent. of the total refractivity is due to the oxygen atoms. Consequently the origin of the strong birefringence must be sought for in the peculiar form of the CO_3 groups. The three oxygen atoms in such a group lie at the corners of an equilateral triangle.

whose side is 2·25 Å, and which in calcite is perpendicular to the trigonal axis of the crystal. The nearest oxygen atoms to any given atom are the two others which are in the same CO_3 group, the next neighbours being at a distance of 3·20 Å. Since the influence of a doublet falls away as the inverse cube of the distance, it follows that an oxygen atom will be influenced to a far greater extent by the other members of its group than it will by atoms in other groups.

Fig. 1 will perhaps make it clear that the CO_3 group will be polarized to a greater extent by a field which is parallel to the plane of the group than by a field of the same strength which is perpendicular to that plane. For reasons to be given later, the carbon atom will be left out of account, and the mutual influence of the three oxygen atoms will alone be considered. In fig. 1 (*a*) the electric field is supposed to be perpendicular to the trigonal axes and to one side of the triangle ABC formed by the oxygen atoms. Each atom is acted on by the external field, and by the field due to its neighbours. In the neighbourhood of A, the field due to the polarized doublets B and C will be in the same direction as the external field, so that the oxygen atom at A will be more strongly polarized than it would be if isolated. In the neighbourhood of B, the field of the doublet at A increases the polarization of the atom at B due to the external field, while the field of the atom at C opposes it; it can readily be seen that on the whole the effect on B is again to increase its polarization. The three oxygen atoms are therefore polarized to a greater extent, owing to each other's presence, than they would be if isolated, and the crystal has a high refractive index for light whose electric vector is in the plane of the group.

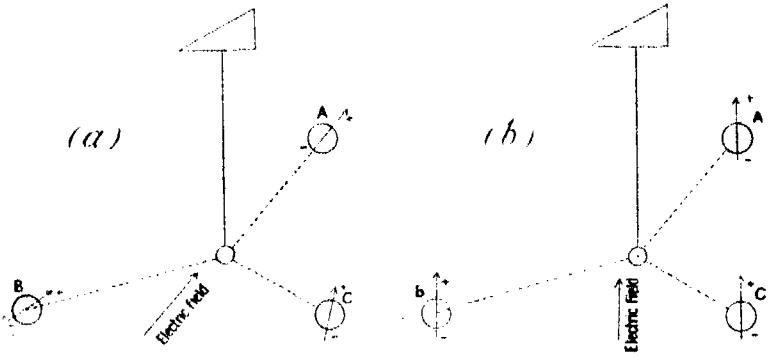

Fig. 1.

On the other hand, when the electric vector is perpendicular to the plane of the group, the polarization of each atom is opposed by the field due to both its neighbours, as a consideration of fig. 1 (*b*) will show. The average polarization of the oxygen atoms is reduced by their mutual influence, and the crystal has a low refractive index for light whose electric vector is perpendicular to the plane of the group. This is in agreement with observation for both calcite and aragonite, the optical properties of which have been already described.

4. In order to calculate the refractive indices of calcite and aragonite, it is necessary to know the extent to which an atom of calcium, carbon, or oxygen becomes polarized under a given electric field, and to know the relative positions of the atoms. The former constants can be deduced from the atomic refractivities of the atoms, estimates of which have been made from the refractive indices of gases, liquids, and solids; the relative positions of the atoms are given by the X-ray analysis. By making the further assumption that the atom, when polarized, has an external field identical with that of an electrical doublet placed at its centre, the absolute values of the refractive indices can be calculated. It will be seen that they are in good agreement with the observed values.

In the formal treatment, the notation of O. W. Richardson's Electron Theory of Matter will be adopted. Electrical charges are expressed in terms of Heaviside units, the repulsion between unit charges at unit distance being equal to $1/4\pi$ dynes.

Under the influence of an electric field, an atom is supposed to develop a doublet of moment se, corresponding to the relative displacement to a distance s of elementary charges $\pm e$. "s" is given by

$$s = E'e\lambda \tag{1}$$

where E' is the strength of the field in the neighbourhood of the atom, and λ is a constant characteristic of the atom. It will be assumed that λ does not depend on the direction of the local electric field; this is not necessarily true for an atom placed in an unsymmetrical position in a crystal, such as the oxygen atom in a CO_3 group, but for the present it will be taken to be the case.

In each cubic centimetre of a polarized dielectric medium, let there be N_1 atoms which form doublets of moment s_1e, N_2 which form doublets of moment s_2e, and so forth. Then it can be shown that

$$(K-1)\bar{E} = P = (N_1es_1 + N_2es_2 + \ldots) \tag{2}$$

where $\bar{E}$ is the average value of the electric intensity throughout the medium, P is the total polarization per unit volume, and K is the dielectric constant of the medium.

Each atom is acted on by the force due to charges in the field, including the doublets of the polarized medium not situated in its immediate neighbourhood. This force is the average electric intensity $\bar{E}$. In addition, it is acted on by the doublets in its immediate neighbourhood. In order to estimate the effect of the neighbouring doublets, a sphere is drawn, with the atom at its centre, which includes a large number of neighbouring atoms. If the doublets included within the sphere be removed, a spherical cavity is left which is positively and negatively charged on opposite faces, owing to the polarization of the medium. These charges create a field equal to $\frac{1}{3}P$ at the centre of the sphere. If the doublets which have been removed from the sphere are distributed at random, it can be shown that their average effect on an atom at the centre is zero. It follows that the local field acting on an atom is $\bar{E} + \frac{1}{3}P$, and that the strengths of the doublets are determined by equations

$$\frac{s_1}{\lambda_1} = \frac{s_2}{\lambda_2} = \ldots = (\bar{E} + \tfrac{1}{3}P)\,e. \tag{3}$$

From equations (2) and (3)

$$P = (\bar{E} + \tfrac{1}{3}P)\,.\,\Sigma Ne^2\lambda.$$

$$K - 1 = \frac{P}{\bar{E}} = \frac{\Sigma Ne^2\lambda}{1 - \frac{1}{3}\Sigma Ne^2\lambda}. \tag{4}$$

This equation remains true when the electric fields are due to light waves. The polarization of each atom is still proportional to the intensity of the electric vector, though of course the effective value of λ depends on the frequency of the light. The equation becomes

$$n^2 - 1 = \frac{\Sigma Ne^2\lambda}{1 - \frac{1}{3}\Sigma Ne^2\lambda} \tag{5}$$

where n is the refractive index of the medium. This equation may be written

$$\frac{n^2 - 1}{n^2 + 2} = \tfrac{1}{3}\Sigma Ne^2\lambda. \tag{6}$$

Since N is proportional to the density ρ of the medium, the well-known Lorentz law follows that $\frac{n^2 - 1}{n^2 + 2} \propto \rho$, a relation which is obeyed with considerable accuracy by isotropic media. If both sides of the equation are multiplied by M/ρ, where M is the molecular weight of the substance, one obtains the equation

$$\frac{M}{\rho} \cdot \frac{n^2 - 1}{n^2 + 2} = a\,(\tfrac{1}{3}N_0 e^2 \lambda_1) + b\,(\tfrac{1}{3}N_0 e^2 \lambda_2) + \dots$$

or

$$R = aA_1 + bA_2 + \dots \tag{7}$$

where N_0 is the Avogadro constant, or number of molecules in a gram molecule, and there are "a" atoms of the first kind, "b" of the second kind, and so on in a molecule. "R" is termed the molecular refractivity of the compound, and A_1, A_2, &c., are termed the atomic refractivities of its constituents. R is a constant characteristic of the compound, whatever its state of aggregation. A_1, A_2 are constants characteristic of the atoms. It is found that this additive law is approximately obeyed by isotropic media, and that it is possible to deduce a series of constants which stand for atomic refractivities. We would expect the law to be exactly obeyed were it not for the fact that all other atoms around any given atom are not arranged at random, since those which form part of the same molecule have a definite relationship to it. It is no longer true that there is no average effect of the doublets within a sphere on an atom at its centre, and the simple relationship breaks down. In order to get accurate values for atomic refractivity it is necessary to take into account the mutual effect of atoms in a molecule; increasing knowledge of molecular structure should make this possible.

The case of a crystal will now be considered. Surrounding each atom is a number of other atoms whose exact positions are known by X-ray analysis. Taking the origin of co-ordinates at the atom under consideration and the x direction as being that of the field in the medium, a doublet at a point xyz whose components of polarization are μ_x, μ_y, μ_z creates a field at the origin whose x component is equal to

$$\frac{\mu_x}{4\pi} \cdot \frac{3x^2 - r^2}{r^5} + \frac{\mu_y}{4\pi} \cdot \frac{3xy}{r^5} + \frac{\mu_z}{4\pi} \cdot \frac{3xz}{r^5}, \tag{8}$$

where

$$r^2 = x^2 + y^2 + z^2.$$

Instead of equations such as

$$\frac{s_1}{\lambda_1} = (\bar{E} + \tfrac{1}{3}P)\,e,$$

a series of equations must be formed of the following type :—

$$\left.\begin{aligned} \frac{s_1}{\lambda_1} &= (\bar{E} + \tfrac{1}{3}P)\,e + (a_1 s_1 e + a_2 s_2 e + \dots)\,e \\ \frac{s_2}{\lambda_2} &= (\bar{E} + \tfrac{1}{3}P)\,e + (b_1 s_1 e + b_2 s_2 e + \dots)\,e, \text{ etc.} \end{aligned}\right\} \tag{9}$$

The term a_1s_1e represents the field due to all the atoms within a sphere of radius r whose doublet strength is s_1e. The coefficient a_1 is calculated by equation (8).

$$a_1 = \sum_{r_0}^{r} \frac{1}{4\pi r^3} \cdot \frac{3x^2 - r^2}{r^2}. \tag{10}$$

Actually, these equations will be complicated by the fact that, although the electric field is in the direction of the x axis, the polarization of the atoms will have components in the y and z directions, and these components in neighbouring atoms will influence the component in the x direction of the atom under consideration. This effect will be allowed for in the numerical calculations which follow.

Equations (9) can be written

$$\frac{s_1}{\lambda_1} = (\bar{E} + \tfrac{1}{3}P)\, e + \frac{s_1}{\lambda_1} a_1 e^2 \lambda_1 + \frac{s_2}{\lambda_2} a_2 e^2 \lambda_2 + \dots.$$

The values of a_1, a_2 are calculated by (10) and the values of λ_1, λ_2 are deduced from atomic refractivities, for which we know approximate values. It is therefore possible to calculate coefficients such as $a_1e^2\lambda_1$, and to solve the equations for s_1/λ_1, s_2/λ_2, etc. In practice it is found that the values of the coefficients $a_1e^2\lambda_1$, $a_2e^2\lambda_2$, are small compared with unity (they are of the order ± 0·1 or ± 0·2 in calcite and aragonite). The solutions of the equations take the form

$$\left.\begin{aligned} \frac{s_1}{\lambda_1} &= C_1 \,.\, (\bar{E} + \tfrac{1}{3}P)\, e \\ \frac{s_2}{\lambda_2} &= C_2 \,.\, (\bar{E} + \tfrac{1}{3}P)\, e, \text{ etc.,} \end{aligned}\right\} \tag{11}$$

where C_1, C_2 are constants not differing greatly from unity. The constants depend on the direction of the electric vector, and it is their variation with this direction which gives rise to the double refraction.

The refractive indices for any given direction of the electric vector can be calculated by an equation similar to (5)

$$n^2 - 1 = \frac{(C_1N_1e^2\lambda_1 + C_2N_2e^2\lambda_2 + \dots)}{1 - \frac{1}{3}(C_1N_1e^2\lambda_1 + C_2N_2e^2\lambda_2 + \dots)}. \tag{12}$$

5. These equations will now be applied to the numerical calculation of the refractive indices. It is first necessary to assign values to the atomic refractivities of the calcium, carbon, and oxygen atoms in calcite and aragonite. The calcium atoms occur as ions, and the value I_{Ca}^{++} assigned by Wasast-

jerna* to these ions is 1·99. The exact value which is taken is not important, since these atoms only contribute about 15 per cent. of the total refractivity. The molecular volumes of calcite and aragonite are 36·13 and 34·01 respectively (Groth), and therefore the product $Ne^2\lambda$ which appears in the expressions for refractive indices (12) has the following values for the calcium atoms

$$\left(Ne^2\lambda = \frac{3\rho}{M} \cdot I_{Ca}^{++} \right) :—$$

Calcite	0·165
Aragonite	0·175

The values to be assigned to the oxygen and carbon atoms will depend on the view adopted as to the structure of the CO_3 group. Wasastjerna (*loc. cit.* p. 5) compares the refractivities of several molecules or ions containing three oxygen atoms.

Al_2O_3	10·6
SO_3	10·8
NO_3^-	10·4
CO_3^{--}	11·1

From the similarity of these figures, he concludes that practically the whole of the refractivity is to be ascribed in each case to the three oxygen atoms. This is in accord with Kossel's view of the nature of these groups. The atoms of aluminium, sulphur, nitrogen, and carbon have lost the electrons of the outer shell to the oxygen atoms, and have become highly charged positive ions in consequence. The inner electronic shell has such small dimensions that the atom makes practically no contribution to the refractivity of the group. The refractivities are to be ascribed to the three oxygen ions O^{--} which are common to all the groups, and the ionic refractivity I_0^{--} must have a value between 3·3 and 3·7.

This view will be adopted; it will be assumed that the carbon atom has a negligible refractivity, and that the oxygen ion has a refractivity of 3·30. The figures for refractivities which have just been given were originally calculated in a way which took no account of the influence of the atoms on each other, hence it is not surprising that they are in imperfect agreement. The calculations made here, where this mutual influence is taken into account, show that the value $\frac{11 \cdot 1}{3}$ or 3·70, is too high an estimate for the ionic refractivity of oxygen in CO_3 groups, and that 3·30 is probably closer to the truth. It may again be emphasized that small variations in the value assigned to the oxygen ions do not greatly affect the *difference* between the refractive indices, which it is our present object to calculate and compare with observation. The values of $Ne^2\lambda$, where N stands for the total number of oxygen atoms in one cubic centimetre, are then as follows:—

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* J. A. Wasastjerna "On the Refraction Equivalents of Ions and Structure of Compound Ions," 'Soc. Scient. Fenn. Comm. Phys. Math.,' 1, 37 (1923).

Calcite	0·822
Aragonite	0·873

In order to illustrate the method of calculation, a first approximation will be made by supposing that

(1) the calcium atoms are polarized to an extent given by the simple equation $s/\lambda = (\bar{E} + \frac{1}{3}P)e$,

(2) the sphere drawn round each oxygen atom, in computing the influence of neighbouring atoms, is of such a size that it only takes in the other oxygen atoms in the same CO_3 group.

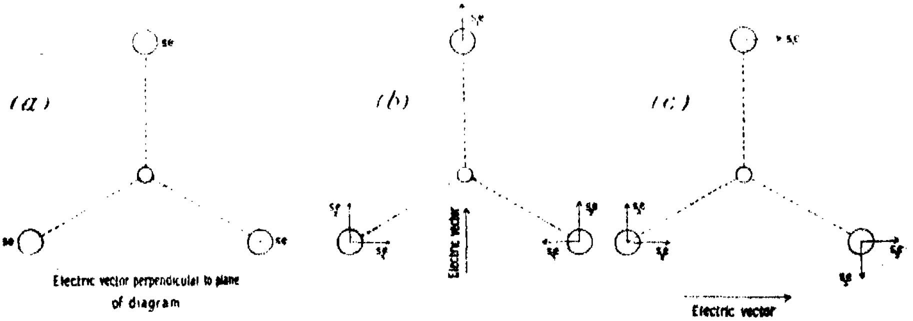

FIG. 2.

In fig. 2 (*a*) the electric vector is at right angles to the plane of the diagram and each oxygen atom is polarized to an extent s given by

$$\frac{s}{\lambda} = (\bar{E} + \tfrac{1}{3}P)e - 2 \cdot \frac{1}{4\pi r_0^3} \cdot se^2 \qquad (13)$$

or

$$\frac{s}{\lambda}\left(1 + \frac{2e^2\lambda}{4\pi r_0^3}\right) = (\bar{E} + \tfrac{1}{3}P)e.$$

Since the ionic refractivity I_0^{--} is to be taken as 3·30, it follows that

$$\tfrac{4}{3}N_0e^2\lambda = 3\cdot30,$$

where N_0 is Avogadro's number $6\cdot062 \times 10^{23}$. The distance r_0 is $2\cdot25$ Å. Therefore

$$\frac{e^2\lambda}{4\pi r_0^3} = \frac{3\,.\,3\cdot30}{6\cdot062\,.\,10^{23}}\,.\,\frac{1}{4\pi\,.\,(2\cdot25)^3\,.\,10^{-24}} = 0\cdot1141.$$

Substituting in (13) one gets

$$\frac{s}{\lambda} = \frac{1}{1\cdot228}\left(\bar{\mathrm{E}} + \tfrac{1}{3}\mathrm{P}\right) = 0\cdot815\left(\bar{\mathrm{E}} + \tfrac{1}{3}\mathrm{P}\right),$$

$$n^2 - 1 = \frac{0\cdot815\,.\,0\cdot822 + 0\cdot165}{1 - \frac{1}{3}(0\cdot815\,.\,0\cdot822 + 0\cdot165)} = 1\cdot155,$$

$$n = 1\cdot468 \text{ (extraordinary ray).}$$

The observed value for the extraordinary ray in calcite is $1\cdot486$.

The equations for fig. 2 (*b*) where the vector lies in the plane of the CO_3 group are as follows :—

$$\frac{s_1}{\lambda} = \left(\bar{\mathrm{E}} + \tfrac{1}{3}\mathrm{P}\right) e + \frac{1}{4\pi r_0^3}\left(2\cdot50 s_2 e + 2\cdot60 s_3 e\right) e,$$

$$\frac{s_2}{\lambda} = \left(\bar{\mathrm{E}} + \tfrac{1}{3}\mathrm{P}\right) e + \frac{1}{4\pi r_0^3}\left(1\cdot25 s_1 e - s_2 e\right) e,$$

$$\frac{s_3}{\lambda} = \frac{1}{4\pi r_0^3}\left(1\cdot30 s_1 e - 2 s_3 e\right) e.$$

These simultaneous equations can be solved in exactly the same way, and lead to the values

$$\frac{s_1}{\lambda} = 1\cdot36\left(\bar{\mathrm{E}} + \tfrac{1}{3}\mathrm{P}\right) e,$$

$$\frac{s_2}{\lambda} = 1\cdot07\left(\bar{\mathrm{E}} + \tfrac{1}{3}\mathrm{P}\right) e,$$

$$\frac{s_3}{\lambda} = 0\cdot163\left(\bar{\mathrm{E}} + \tfrac{1}{3}\mathrm{P}\right) e.$$

To calculate the corresponding refractive index, the mean polarization of the oxygen atoms $\frac{s_1 + 2s_2}{3}e$ in the direction of the field must be taken. This is given by

$$\frac{s_1 + 2s_2}{3\lambda} = 1\cdot17\left(\bar{\mathrm{E}} + \tfrac{1}{3}\mathrm{P}\right) e.$$

From this the value of the refractive index can be calculated to be $1\cdot676$, the observed value being $1\cdot658$. Thus it will be seen that the influence of the oxygen atoms on each other gives an effect of the right order to explain the birefringence in calcite.

The equations for fig. 2 (*c*) where the electric vector is parallel to the base of the triangle have a different form, but they lead to the same equation, $\frac{s_1 + 2s_2}{3\lambda} = 1\cdot17\,(\bar{E} + \frac{4}{3}P)\,e$. This is a necessary consequence of the symmetry of the group. Since it has a trigonal axis, the average polarization for a vector in any direction in the plane of the group must be the same.

The refractive indices of aragonite can be calculated in the same way. The results are summarized in the following table :—

		Calculated.	Observed.
Calcite	ε	1·468	1·486
	ω	1·676	1·658
Aragonite	α	1·503	1·530
	β	1·730	1·681
	γ	1·730	1·686

6. In order to calculate the refractive indices more accurately, one must take into consideration the influence on each atom of a large number of neighbouring atoms. This can be done by describing a sphere of large radius around each atom, and summing the effect of all the doublets included within the sphere. This should be done so as to include the effect of oxygen on oxygen, oxygen on calcium, calcium on oxygen, and calcium on calcium. Components of polarization at right angles to the average field should be considered. A number of simultaneous equations will give the resulting average polarization for each direction of the electric vector.

Since the oxygen atoms are three times as numerous as the calcium atoms, and polarized almost to twice the extent, the effect of oxygen on oxygen will be the most important. To carry out the process described in the preceding paragraph by direct computation is laborious, when a large number of neighbouring doublets are taken into account, and it is probable that the application of mathematical analysis will prove to be the shortest way of getting accurate results. In order to get some idea of the effect of carrying out the calculation more carefully, the following procedure has been adopted :—

(*a*) A sphere of 6 Å radius has been drawn round each oxygen atom, and the effect on that atom of all oxygen doublets within the sphere has been summed up. Such a sphere includes 42 neighbouring atoms in calcite and 50 in aragonite. The components of polarization which are not in the direction of the field have been neglected, except those of the two nearest oxygen atoms in the same CO_3 group. The equation in the last paragraph shows how weak

s_2 is, so that no large error will be introduced by neglecting it for distant atoms.

(*b*) The effect of the calcium atoms on the oxygen atoms has been neglected. Calculation of its effect on ε in calcite shows that in this case it only affects the refractive index in the third decimal place, and much larger errors than this are introduced in other ways.

(*c*) The calcium atoms are supposed to be polarized as if they were in an isotropic medium. Though this will not be the case, their smaller number and weaker polarization makes it justifiable to neglect the effect on them of neighbouring doublets within a sphere.

The effect of the procedure can be illustrated by the case of calcite when the electric vector is perpendicular to the plane of the CO_3 group (extraordinary ray). One may imagine a sphere of ever-increasing radius to be drawn round an oxygen atom, and the field due to the doublets inside it summed up for each value of the radius. When the radius exceeds 2·25 Å (r_0), the other two oxygen atoms of its own group produce an effect

$$\frac{1}{4\pi r_0^3} \cdot 2se,$$

which is given a negative sign because it opposes $(\bar{E} + \frac{1}{3}P)$. Between 3 Å and 3·5 Å a set of doublets are included which produce on the whole a positive effect, which half cancels the first negative effect. Another group between 4 Å and 4·5 Å gives a small positive effect, groups between 4·5 Å and 5·5 Å give large negative effects, and another between 5·5 Å and 6 Å a small positive effect. The final result is embodied in the equation

$$\frac{s}{\lambda} = (\bar{E} + \tfrac{1}{3}P)\,e - \frac{1}{4\pi r_0^3} \cdot 1{\cdot}52se^2,$$

instead of the equation (13) on page 378,

$$\frac{s}{\lambda} = (\dot{E} + \tfrac{1}{3}P) - \frac{1}{4\pi r_0^3} \cdot 2se^2.$$

The former process of only considering oxygen atoms in the same group has obviously led to an exaggerated estimate of the influence of neighbouring doublets.

In general, the effect of taking into account a large number of neighbouring atoms is of the same nature as the above. The estimate of the influence of neighbouring atoms is in every case reduced, but is not reversed in sign. It is clear, however, that even when 50 neighbouring doublets are included in the sphere, the final result is far from accurate. The calculated effect depends on the radius chosen for the sphere, and at 6 Å is varying either way by 10 per cent. or 15 per cent. as the increasing sphere includes fresh groups of doublets. Too close an agreement between calculated and observed values must not, therefore, be expected, since these variations alter the calculated refractive index by 0·01 or 0·02. The equations* for the polarization of the oxygen atom which have been computed in this way are as follows :—

Calcite.—Polarization parallel to trigonal axis

$$\frac{s}{\lambda} = \mathrm{E}e - \frac{1}{4\pi r_0{}^3} \cdot 1 \cdot 52 s e^2,$$

whence

$$\frac{s}{\lambda} = 0 \cdot 847 \mathrm{E}e.$$

Polarization perpendicular to trigonal axis

$$\frac{s_1}{\lambda} = \mathrm{E}e + \frac{1}{4\pi r_0{}^3}(1 \cdot 83 s_2 e^2 - 0 \cdot 38 s_1 e^2 + 2 \cdot 6 s_3 e^2),$$

$$\frac{s_2}{\lambda} = \mathrm{E}e + \frac{1}{4\pi r_0{}^3}(1 \cdot 01 s_1 e^2 - 0 \cdot 84 s_2 e^2),$$

$$\frac{s_3}{\lambda} = \frac{1}{4\pi r_0{}^3}(1 \cdot 30 s_1 e^2 - 2 s_3{}^2),$$

whence
$$\frac{s_1 + 2s_2}{3\lambda} = 1 \cdot 100 \mathrm{E}e.$$

Aragonite.—Polarization parallel to *a* axis

$$\frac{s_1}{\lambda} = \mathrm{E}e + \frac{1}{4\pi r^3_0}(0 \cdot 59 s_1 e^2 - 1 \cdot 57 s_2 e^2 + 2 \cdot 60 s_3 e^2),$$

$$\frac{s_2}{\lambda} = \mathrm{E}e + \frac{1}{4\pi r_0{}^3}(-0 \cdot 70 s_1 e^2 + 2 \cdot 11 s_2 e^2),$$

$$\frac{s_3}{\lambda} = \frac{1}{4\pi r_0{}^3}(1 \cdot 30 s_1 e^2 + s_3 e^2),$$

whence
$$\frac{s_1 + 2s_2}{3\lambda} = 1 \cdot 118 \mathrm{E}e.$$

Polarization parallel to *b* axis

$$\frac{s_1}{\lambda} = \mathrm{E}e + \frac{1}{4\pi r_0{}^3}(-0 \cdot 10 s_1 e^2 + 2 \cdot 01 s_2 e^2 + 2 \cdot 60 s_3 e^2),$$

$$\frac{s_2}{\lambda} = \mathrm{E}e + \frac{1}{4\pi r_0{}^3}(0 \cdot 83 s_1 e^2 - 0 \cdot 93 s_2 e^2),$$

$$\frac{s_3}{\lambda} = \frac{1}{4\pi r_0{}^3}(1 \cdot 30 s_1 e^2 - 2 s_3 e^2),$$

---

* In these equations "E" has been used as an abbreviation for "$(\mathrm{E} + \frac{1}{3}\mathrm{P})$."

whence

$$\frac{s_1 + 2s_2}{3\lambda} = 1\cdot100\mathrm{E}e.$$

Polarization parallel to c axis

$$\frac{s_1}{\lambda} = \mathrm{E}e - \frac{1}{4\pi r_0{}^3}(0\cdot36s_1e^2 + 0\cdot52s_2e^2),$$

$$\frac{s_2}{\lambda} = \mathrm{E}e - \frac{1}{4\pi r_0{}^3}(0\cdot25s_1e^2 + 1\cdot14s_2e^2),$$

whence

$$\frac{s_1 + 2s_2}{3\lambda} = 0\cdot874\mathrm{E}e.$$

The refractive indices can be calculated by using these values for the average polarization of the oxygen atoms. They are compared with the actual values in the following table :—

		Calculated.	Observed.
Calcite	ϵ	1·488	1·486
	ω	1·631	1·658
Aragonite	α	1·538	1·530
	β	1·694	1·681
	γ	1·680	1·686

The agreement between calculated and observed values is not very close, but it has been improved by the more complete analysis, and is within the error of calculation. The inaccurate nature of the analysis is shown by the fact that β is calculated to be greater than γ for aragonite, whereas it should be less. When it is recalled that the refractivities of calcium and oxygen have been computed from quite different compounds (CaF_2, SO_3, Al_2O_3, etc.), and that no assumptions other than those of the dielectric theory have been made, it is justifiable to regard the general agreement as satisfactory.

These results have been obtained by identifying the position of the doublet with the centre of the atom as found by X-ray analysis. The estimate of 1·30 Å for the distance between carbon and oxygen centres may be slightly too large, but it cannot be far from the truth, since the mutual effect varies as the inverse cube of the distance between oxygen atoms, and any large error would destroy the agreement between calculation and observation.

7. Many carbonates and nitrates crystallize like calcite or aragonite, and display strong double refraction. A general survey of the refractive indices shows that the birefringence is satisfactorily explained in each case by the

effect of the oxygen doublets on each other. It is convenient to express the indices in the form of molecular refractivities $\left(R = \frac{M}{\rho} \cdot \frac{n^2 - 1}{n^2 + 2}\right)$ for the ordinary and extraordinary ray. The orthorhombic crystals of aragonite type are nearly uniaxial, and have been treated as if they had a mean index of $\frac{1}{2}(\beta + \gamma)$ for the ordinary ray. The indices for the rhombohedral carbonates are taken from a very complete series of measurements by M. Gaubert.*

Calcite series.

—	M/ρ.	ω.	ϵ.	R_ω.	R_ϵ.	$R_\omega - R_\epsilon$.	R'_ω.	R'_ϵ.
$MgCO_3$	27·57	1·717	1·515	10·83	8·30	2·53	10·39	7·86
$ZnCO_3$........	27·97	1·872	1·618	12·72	9·79	2·93	11·02	8·09
$FeCO_3$........	22·65	1·872	1·632	13·48	10·57	2·91	*11·19*	*8·28*
$MnCO_3$	31·19	1·815	1·597	13·52	10·62	2·90	*11·19*	*8·29*
$\frac{Mg}{2}\frac{Ca}{2}CO_3$	32·00	1·682	1·503	12·10	9·44	2·66	10·89	8·23
$CdCO_3$........	34·51	?	?					
$CaCO_3$........	36·13	1·658	1·486	13·31	10·37	2·94	11·32	8·38

The last two columns give the refractivities due to the oxygen atoms, when that due to the metal atoms has been subtracted. The refractivities of the metal ions are taken to be

$$I_{Mg} = 0{\cdot}44,\quad I_{Ca} = 1{\cdot}99,\quad I_{Sr} = 3{\cdot}22,\quad I_{Ba} = 5{\cdot}24,\quad I_{\frac{Mg}{2}\frac{Ca}{2}} = 1{\cdot}22,$$

$$I_{Mn} = 2{\cdot}33,\quad I_{Fe} = 2{\cdot}29,\quad I_{Zn} = 1{\cdot}70,\quad I_{Pb} = 9{\cdot}93.$$

With the exception of iron and manganese, these values are taken from Wasastjerna's tables. The values for iron and manganese are chosen so as to fit in with the other figures. For calcite, we have calculated that

$$R'_\omega = 10{\cdot}88, \qquad R'_\epsilon = 8{\cdot}38.$$

The values of R'_ω and R'_ϵ are in the neighbourhood of these estimates for all the carbonates. The effect of neighbouring atoms will depend, of course, on structure and should be recalculated for each crystal. The CO_3 group probably retains the same form, however, and the crystal structures are very similar, so that the effect of neighbouring doublets will not vary very much from crystal to crystal. So it may be said that the explanation of the birefringence of calcite may be extended to the other rhombohedral carbonates.

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* "Sur les indices de réfraction des carbonates rhomboédriques," P. Gaubert, 'Bull. Soc. Fr. Min.,' p. 88 (1919).

Aragonite Series.

	$\frac{M}{\rho}$.	$\frac{\beta+\gamma}{2}$.	α.	$R_{\frac{\beta+\gamma}{2}}$	R_α.	Diff.	$R'_{\frac{\beta+\gamma}{2}}$	R'_α.
$CaCO_3$	34·01	1·683	1·530	12·91	10·51	2·40	10·92	8·52
$SrCO_3$	39·87	1·658	1·514	14·71	12·00	2·71	11·49	8·78
$PbCO_3$.......	40·44	2·077	1·804	21·20	17·34	3·92	11·27	7·41

These values also fit in with the calculated results, except in the case of lead, where the high refractivity of the lead atom may be the cause of the discrepancy. In the lead carbonate, more of the refractivity is due to the lead atoms than to the oxygen atoms, so that calculations based on the mutual influence of oxygen atoms alone must be very inaccurate. It is to be hoped that more accurate estimates of atomic refractivity, particularly when they are high as in the case of lead, will be possible when calculated in the way indicated in this paper.

Sodium nitrate, which crystallizes like calcite, has very strong birefringence ($\omega = 1\cdot586$, $\epsilon = 1\cdot336$). It would seem that the oxygen atoms in the NO_3 group must be closer together than they are in the CO_3 group in order to account for the strong double refraction.

In conclusion, reference may be made to another series of crystals, though what follows must be regarded as highly speculative, since these crystals have in no case been satisfactorily analyzed by X-rays. The sulphates, in contrast with the carbonates, are distinguished by their very weak birefringence. May not this be due to a tetrahedral arrangement of the four oxygen ions around a central sulphur ion S^{+++}_{+++} in the SO_4 group ? Such an arrangement would be optically isotropic, being equally polarized by an electric vector in any direction.

Further, it can readily be calculated that the average polarization of the oxygen atoms in such a group differs very little from that of four isolated atoms. The figures for $SrSO_4$ and $BaSO_4$ are

	$\frac{M}{\rho}$.	$\frac{\alpha+\beta}{2}$.	γ.	$R_{\frac{\alpha+\beta}{2}}$.	R_γ.	$R'_{\frac{\alpha+\beta}{2}}$.	R'_γ.
$SrSO_4$	46·18	1·6228	1·6310	16·28	16·47	13·06	13·25
$BaSO_4$.....................	51·96	1·6375	1·6491	18·60	18·92	13·36	13·68

The refractivities $R'_{\frac{\alpha+\beta}{2}}$, $R'\gamma$, refer to the SO_4 group and their mean value is 13·36. Since the average mutual influence of the oxygen atoms on each other is small, this leads to a value for the refractivity of the O^{--} ion of 13·36/4 or 3·34, which is in close agreement with the value 3·30 deduced from the carbonates. Most compounds with an acid radical of the form RO_4 display weak birefringence, and a tetrahedral arrangement of oxygen atoms may be the cause of the small difference in the principal refractive indices.

Summary.

Calcite and aragonite, two crystalline forms of calcium carbonate, are closely related in their optical properties. Both crystals possess strong negative birefringence, and their refractivities are nearly identical when allowance is made for the small difference in molecular volume between the two. The crystals have been analyzed by X-ray methods.

The strong double refraction is to be ascribed to the peculiar form of the CO_3 group. This consists of three oxygen atoms grouped around a central carbon atom and lying in a plane. The oxygen atoms are more highly polarized by an electric field than the other atoms in the crystal. The three atoms in the same CO_3 group, when they become electrical doublets, exert a strong influence on each other, which results in their being more strongly polarized by an electric field parallel to the plane of the group than by a field perpendicular to the plane of the group. Hence the refractive index of the crystal is greater when the electric vector is perpendicular to the trigonal axis of calcite than when it is parallel to the axis. The same holds for the pseudohexagonal axis of aragonite.

A numerical calculation of the effect shows that it accounts quantitatively for the difference in refractive indices, both for calcite and aragonite. Values for the refractivities of the calcium and oxygen atoms are assumed which are based on the refractivity of a number of compounds. When these are substituted in the formulæ which are derived, the calculated values of the refractive indices do not differ by more than 1 or 2 per cent. from the observed values.

I wish to express my indebtedness to Prof. O. W. Richardson, who very kindly checked the formulæ used in this paper, and to Sir Henry Miers, who supplied me with references to measurements of refractive index.

Thermodynamics of Electron Emission.

By O. W. Richardson, F.R.S., Wheatstone Professor of Physics in the University of London, King's College.

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1. *Introduction.*

The following paper deals with some applications of thermodynamics to the electron atmospheres in equilibrium with matter. The treatment is a development of earlier papers* and the former ground is traversed again to a certain extent. This has become especially desirable because recent improvements in technique are enabling some of the finer points of the theory to be tested by experiment. In the discussion I keep throughout to electron atmospheres which are so attenuated that the forces exerted by the electrons on each other are quite negligible. I am in no way concerned with the interesting complications which arise when this condition is not satisfied. The theory of these effects is discussed fully by v. Laue.†

The principal quantities dealt with are p the pressure of the electrons in the atmosphere in equilibrium with the substance, V the intrinsic potential at a point just outside the substance, w the latent heat of evaporation (per electron) and T the absolute temperature. The remaining quantities will be indicated as they arise.

I shall consider first of all the changes, if any, which we may expect in thermionic emission at melting and transition points.

2. *Thermionic Emission at Melting and Transition Points.*

I shall deal first with the information which is obtainable by a consideration of isothermal equilibrium at a transition point. Let T_0 be a temperature at which two condensed phases are in equilibrium with the vapour. T_0 may be the melting point or a temperature at which two solid phases are in equilibrium. Indicate the quantities referring to the respective phases by the suffixes 1 and 2. Suppose we have an enclosure at temperature T_0 which contains the phases 1 and 2, the vapour and the accompanying electron atmosphere, but is otherwise vacuous. It can be shown in the usual way that the equilibrium of the electron atmosphere in the field due to the intrinsic potentials requires that

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* Especially 'Phil. Mag.,' vol. 23, p. 263 (1912). *Cf.* also "Electron Theory of Matter," chaps. 17 and 18, and "Emission of Electrons from Hot Bodies," chaps. 2 and 5. These contain references to the literature generally.

† 'Jahrb. d. Radioakt. u. Elektronik.,' vol. 15, p. 205 (1918).

$$\log p_1 - \log p_2 = e\,(V_2 - V_1)/kT_0 \tag{1}$$

where e is the electron charge, k Boltzmann's constant, and p_1 and p_2 are the electron pressures just outside the condensed phases. This relation is independent of interaction between the electrons and the gas phase.

Another relation may be got by separating the atmospheres of the two condensed phases by a non-conducting wall fitted with a cylinder and piston. The condensed phases are now supposed in contact at some point. By allowing a motion of the piston, electrons may be forced from phase 1 into phase 2 and back through the junction. The details of the process are the same as those described in 'Phil. Mag.,' vol. 23, p. 274 (1912), except that there are two condensed phases instead of one and the whole system is at the uniform temperature T_0. Since the cycle considered is reversible and is also isothermal the total heat absorbed in it is zero, which gives

$$w_1 + e\,(V_2 - V_1) - w_2 + e\,P_{21} = 0, \tag{2}$$

where P_{21} is the heat absorbed when unit electric charge crosses from one condensed phase to the other across the boundary and may, subject to certain reservations,* be identified with the Peltier coefficient.

Equations having a formal resemblance to (2) may be written down for the potential discontinuities and the electromotive forces at the interfaces, but as they introduce new quantities they do not help forward the problem immediately under consideration.

Equations (1) and (2) can confidently be regarded as rigorous, as they are derived from the consideration of isothermal cycles which are strictly reversible. They are, however, only valid at the single temperature (or set of single temperatures) T_0. At other temperatures they dissolve into $P_{21} = 0$, $w_1 = w_2$, $V_1 = V_2$ and $p_1 = p_2$. They cannot therefore be differentiated with respect to T.

To obtain further useful information it appears to be necessary to consider systems whose parts are at different temperatures. The simplest way of doing this involves a process similar to that used in obtaining equation (2) except that now the phase 2 is at a temperature $T_2 > T_0$ and the phase 1 is at a temperature $T_1 < T_0$, the two phases being joined by an insulated rod of the same material whose temperature varies from T_2 to T_1.

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* *Cf.*, 'Electron Theory of Matter,' 2nd edn., p. 456.

This part of the calculation suffers from the same type of limitations as Kelvin's theory of thermoelectricity. The flow of heat from the phase at T_2 to that at T_1 presents an irreversible phenomenon inherent in the system. The assumption that the laws of thermodynamics as they apply to reversible cycles can be applied to reversible effects superposed on such a system is one which has never been proved to be necessarily valid.* The conclusions of this part of the calculation cannot therefore be regarded as logically necessary; they are to be regarded rather as suggestive or, at most, highly probable.

On the other hand, in spite of this logical flaw, I believe the results of these calculations are substantially correct; so substantially, in fact, that I feel that any appreciable discrepancies likely to arise in applying them to thermionic phenomena will originate in other directions, in the more immediate future at any rate. The calculations have led to a large body of interdependent and mutually consistent formulæ which are not at any point in conflict with the experimental evidence on the thermionic side, so far as I am able to judge. On the thermoelectric side the results are the same as those of Kelvin's theory. There is no doubt room for much difference of opinion as to whether Kelvin's theory is adequate to embrace the facts of thermoelectricity. My personal judgment on this point is that the value of some of the alleged evidence against it has been over-estimated. There is, I think, general agreement that there is some correspondence between the results of Kelvin's theory and the facts in this domain. Even if this were all that could be claimed it would be sufficient to make the present theory useful from the point of view of thermionics; for the reason that the thermoelectric effects are, as it were, small excrescences of the thermionic. In the thermionic formulæ the thermoelectric quantities play the part of second order terms. The theory could go quite wrong as to them and still be correct, for practical purposes, when applied to the thermionic terms.

There are ways of turning this difficulty about irreversibility. I do not wish to discuss them here as I am not fully satisfied about some of the points to which they lead. They do not, however, appear to indicate anything substantially different from the results of the method under discussion, which is much simpler to handle as a means of calculation.

We now carry out a cyclic transference of electrons similar to that adopted in deducing equation (2) except that now $T_2 > T_0 > T_1$. In general V_1 and V_2 will be unequal. Suppose $eV_1 > eV_2$. Surround the phase at T_2

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* *Cf.* Bohr, 'Phil. Mag.,' vol. 23, p. 984 (1912); Boltzmann, 'Sitzungsber. d. Wien. Akad. d. Wiss.,' math-nat. Kl., Bd. 96, Abt. 2, p. 1258 (1887).

by a restraining field to bring the escaping electrons to the same potential V_1 as those in the T_1 atmosphere. The effect of this restraining field is to raise the internal latent heat of the electrons which escape through it by an amount $e(V_1 - V_2)$. Now allow N electrons to be removed at constant pressure from the phase at T_2. The work done in this operation is NkT_2 and the heat absorbed is $N (w_2 + e\,\overline{V_1 - V_2} + kT_2)$. These electrons are next allowed to expand adiabatically until their temperature falls from T_2 to T_1. This involves an amount of work $= N\,k(T_2 - T_1)/(\gamma-1)$ and the absorption of heat is zero. The electrons are now allowed to expand isothermally at temperature T_1 until their pressure falls to p_1. The work done here is $NkT_1 \log \frac{p_0}{p_1}\left(\frac{T_1}{T_2}\right)^{\gamma/\gamma-1}$ where $\log p_0 = \log p_2 + e\,(V_2 - V_1)/kT_2$ and an equal amount of heat is absorbed. The electrons are now allowed to pass into the condensed phase at T_1 involving work $-NkT_1$ and heat absorption $-N\,(w_1 + kT_1)$. They are now allowed to return from the phase at T_1 to that at T_2 by passing down the connecting portion of varying temperature. This involves an amount of work NEe, where E is the electromotive force in the unequally heated condensed substance, and an absorption of heat equal to

$$e\int_{T_0}^{T_2} \sigma_2 dT + e\int_{T_1}^{T_0} \sigma_1 dT + eP_{12}$$

where σ_2 and σ_1 are the quantities of reversible heat absorved when unit quantity of electricity moves against unit rise of temperature in the two respective phases and P_{12} is the quantity of heat similarly developed in crossing the junction between the two phases. If the second law of thermodynamics is applied to this cycle in the form $\int dQ/T = 0$ we obtain

$$w_2/T_2 - w_1/T_1 + k\log p_2/p_1 - \frac{k\gamma}{\gamma-1}\log T_2/T_1$$
$$+ e\int_{T_0}^{T_2} \frac{\sigma_2}{T}\,dT + e\int_{T_1}^{T_0} \frac{\sigma_1}{T}\,dT + \frac{eP_{12}}{T_0} = 0. \quad (3)$$

If now T_2 and T_1 both approach T_0 we obtain

$$w_2{}^0/T_0 - w_1{}^0/T_0 + k\log p_2{}^0/p_1{}^0 + eP_{12}/T_0 = 0 \quad (4)$$

as the condition holding at the transition point T_0. This agrees with equations (1) and (2). If we substitute the value of P_{12} from (4) in (3)

$$w_2/T_2 - w_2{}^0/T_0 + k\log p_2/p_2{}^0 - \frac{k\gamma}{\gamma-1}\log T_2 + e\int_{T_0}^{T_2} \frac{\sigma_2}{T}\,dT$$
$$= w_1/T_1 - w_1{}^0/T_0 + k\log p_1/p_1{}^0 - \frac{k\gamma}{\gamma-1}\log T_1 + e\int_{T_0}^{T_1} \frac{\sigma_1}{T}\,dT. \quad (5)$$

The left-hand side contains only quantities referring to phase 2 (suffix 2) and on the right-hand side all the quantities refer to phase 1 (suffix 1). Therefore the quantity

$$w/\mathrm{T} - w_0/\mathrm{T}_0 + k \log p/p_0 - \frac{k\gamma}{\gamma - 1} \log \mathrm{T} + e \int_{\mathrm{T}_0}^{\mathrm{T}} \frac{\sigma}{\mathrm{T}}\, d\mathrm{T}$$

is invariant both in T and the phase. If T approaches T_0 it reduces to $\frac{k\gamma}{\gamma - 1} \log \mathrm{T}_0$; so that

$$w/\mathrm{T} - w_0/\mathrm{T}_0 + k \log p/p_0 - \frac{k\gamma}{\gamma - 1} \log \mathrm{T}/\mathrm{T}_0 + e \int_{\mathrm{T}_0}^{\mathrm{T}} \frac{\sigma}{\mathrm{T}}\, d\mathrm{T} = 0. \qquad (6)$$

for every T and either phase. If $\mathrm{T} < \mathrm{T}_0$ and if in addition T_0 is the lowest transition point which the substance possesses then we can put without ambiguity

$$\int_{\mathrm{T}_0}^{\mathrm{T}} \frac{\sigma}{\mathrm{T}}\, d\mathrm{T} = \int_0^{\mathrm{T}} \frac{\sigma}{\mathrm{T}}\, d\mathrm{T} - \int_0^{\mathrm{T}_0} \frac{\sigma}{\mathrm{T}}\, d\mathrm{T} \qquad (7)$$

and from (6)

$$w_0/\mathrm{T}_0 + k \log p_0 - \frac{k\gamma}{\gamma - 1} \log \mathrm{T}_0 + e \int_0^{\mathrm{T}_0} \frac{\sigma}{\mathrm{T}}\, d\mathrm{T}$$
$$= w/\mathrm{T} + k \log p - \frac{k\gamma}{\gamma - 1} \log \mathrm{T} + e \int_0^{\mathrm{T}} \frac{\sigma}{\mathrm{T}}\, d\mathrm{T}. \qquad (8)$$

Now the right-hand side of (8) is equal to a universal constant* which we will denote by C_1. A critical examination of this statement will be given below (§ 3). We see from (8) that

$$w/\mathrm{T} + k \log p - \frac{k\gamma}{\gamma - 1} \log \mathrm{T} + e \int_0 \frac{\sigma}{\mathrm{T}}\, d\mathrm{T} = \mathrm{C}_1 \text{ a universal constant}, \qquad (9)$$

holds for the lowest temperature phase at all temperatures between zero and the transition point.

If $\mathrm{T} > \mathrm{T}_0$ (7) will still hold provided we understand by σ in the integrals on the right-hand side the value of σ which is appropriate to the substance at temperature T for the phase which is proper to that temperature. With this interpretation, and denoting by dashes the quantities appropriate to the higher temperature phase, we have from (6)

$$w'/\mathrm{T} + k \log p' - \frac{k\gamma}{\gamma - 1} \log \mathrm{T} + e \int_0^{\mathrm{T}} \frac{\sigma}{\mathrm{T}}\, d\mathrm{T}$$
$$= w_0'/\mathrm{T}_0 + k \log p_0' - \frac{k\gamma}{\gamma - 1} \log \mathrm{T}_0 + e \int_0^{\mathrm{T}_0} \frac{\sigma}{\mathrm{T}}\, d\mathrm{T}. \qquad (10)$$

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* *Cf.* O. W. Richardson, 'Royal Soc. Proc.,' A, vol. 91, p. 530 (1915).

But from (8) or (9)

$$e\int_0^{T_0}\frac{\sigma}{T}\,dT - \frac{k\gamma}{\gamma-1}\log T_0 = C_1 - w_0/T_0 - k\log p_0$$

so that

$$\begin{aligned} w'/T + k\log p' - \frac{k\gamma}{\gamma-1}\log T + e\int_0^T\frac{\sigma}{T}\,dT & \\ = C_1 + w_0'/T_0 - w_0T_0 + k\log p_0'/p_0 & \\ = C_1 - eP_{10}/T_0 & \qquad (11) \end{aligned}$$

from (1) and (2).

By an extension of the argument, we see that if there are a number of transition points the universal constant C_1 in (9) will be replaced by

$$C_1 - \Sigma eP_t/T_t \qquad (12)$$

where the summation is extended over all the transition points below the temperature T.

In general we find that the pressure of the electrons in equilibrium with any phase is given by

$$p = e_1^{\frac{1}{k}[C_1 - \Sigma eP_t/T_t]}\,T^{\frac{\gamma}{\gamma-1}}\,e_1^{-w/kT - e\int_0^T\frac{\sigma}{kT}dT} \qquad (13)$$

where e_1 is written for the base of the natural logarithms, to distinguish from the electronic charge e; C_1 is the universal constant mentioned already, P_t is the heat liberated when unit charge passes across the junction between two successive phases at their transition temperature T_t, w is the internal latent heat of evaporation of the electrons at the actual temperature T, and in the integral, σ, which may be discontinuous at the transition points, is the actual value at every T for the phase which exists at that temperature.

I have shown* that the Clausius-Clapeyron treatment applied to electron emission leads to the equation

$$p = kTAe_1^{\int_0^T\frac{\phi}{kT^2}dT}. \qquad (14)$$

As a general proof that the latent heat ϕ, which enters into equation (14), is completely identical with the latent heat w of the preceding equations has, so far as I am aware, never been devised, we shall keep the two symbols distinct. In general all we are entitled to say about A in (14) is that it is independent of T, but may be characteristic of the substance.

In view of the fact that ϕ may be discontinuous at the transition points the integral $\int_0^T\frac{\phi}{kT^2}dT$ will require careful consideration. Below the lowest transition point it is unambiguous and, replacing the pressure p by the equivalent concentration ν, we write

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* 'Phil. Mag.,' vol. 23, p. 619 (1912).

$$\nu = \mathrm{A}e_1^{\int_0^{\mathrm{T}} \frac{\phi}{k\mathrm{T}^2} d\mathrm{T}} \tag{15}$$

as valid for all temperatures T below the lowest transition point T_1, A being independent of T, but possibly taking different values for different substances. At T_1, ϕ may be discontinuous, and for the phase between T_1 and the next transition point T_2 we write

$$\begin{aligned} \nu &= \mathrm{A}_1 e_1^{\int_{\mathrm{T}_1}^{\mathrm{T}} \frac{\phi}{k\mathrm{T}^2} d\mathrm{T}} \\ &= \mathrm{A} \cdot \frac{\mathrm{A}_1}{\mathrm{A}} \cdot e_1^{-\left|\frac{\phi}{k\mathrm{T}}\right|_{\mathrm{T}'_1}^{\mathrm{T}} + \int_{\mathrm{T}'_1}^{\mathrm{T}} \frac{1}{k\mathrm{T}} \frac{d\phi}{d\mathrm{T}} d\mathrm{T}}. \end{aligned} \tag{16}$$

The dashes affixed to the symbols indicate that at a discontinuity the value on the high temperature side is to be taken. When the limit is T_1 instead of T'_1, the value on the low temperature side is to be understood. The integrals are to be understood as broken up at each transition point, so that each integral only covers a range where the integrand is continuous. Above the m^{th} transition point we shall have instead of (16)

$$\begin{aligned} \nu &= \mathrm{A} \cdot \frac{\mathrm{A}_1}{\mathrm{A}} \cdot \frac{\mathrm{A}_2}{\mathrm{A}_1} \cdots \frac{\mathrm{A}_m}{\mathrm{A}_{m-1}} \cdot e_1^{-\left|\frac{\phi}{k\mathrm{T}}\right|_{\mathrm{T}'_m}^{\mathrm{T}} + \int_{\mathrm{T}'_m}^{\mathrm{T}} \frac{1}{k\mathrm{T}} \frac{d\phi}{d\mathrm{T}} d\mathrm{T}} \\ &= \mathrm{A} \cdot \frac{\mathrm{A}_1}{\mathrm{A}} \cdot \frac{\mathrm{A}_2}{\mathrm{A}_1} \cdots \frac{\mathrm{A}_m}{\mathrm{A}_{m-1}} \cdot e_1^{\frac{\phi_m}{k\mathrm{T}_m} - \int_0^{\mathrm{T}_m} \frac{1}{k\mathrm{T}} \frac{d\phi}{d\mathrm{T}} d\mathrm{T}} \cdot e_1^{-\frac{\phi}{k\mathrm{T}} + \int_0^{\mathrm{T}} \frac{1}{k\mathrm{T}} \frac{d\phi}{d\mathrm{T}} d\mathrm{T}} \end{aligned} \tag{17}$$

From (15) we see that in the lowest temperature phase (phase (1)) at $\mathrm{T} = \mathrm{T}_1$ we have

$$\nu = \nu_{11} = \mathrm{A}e_1^{\int_0^{\mathrm{T}_1} \frac{\phi}{k\mathrm{T}} d\mathrm{T}}.$$

At the same temperature T_1 but in the higher temperature phase (phase (2)) we have, from (16),

$$\nu = \nu_{12} = \mathrm{A} \cdot \frac{\mathrm{A}_1}{\mathrm{A}}.$$

At T_2 in phase 2 we have, from (16),

$$\nu = \nu_{22} = \mathrm{A} \cdot \frac{\mathrm{A}_1}{\mathrm{A}} \cdot e_1^{\int_{\mathrm{T}'_1}^{\mathrm{T}_2} \frac{\phi}{k\mathrm{T}^2} d\mathrm{T}}.$$

At T_2 in phase 3 we have, from (17),

$$\nu = \nu_{23} = \mathrm{A} \cdot \frac{\mathrm{A}_1}{\mathrm{A}} \cdot \frac{\mathrm{A}_2}{\mathrm{A}_1}$$

and so on. Generally

$$\nu = \nu_{mm} = \mathrm{A} \,.\, \frac{\mathrm{A}_1}{\mathrm{A}} \,.\, \frac{\mathrm{A}_2}{\mathrm{A}_1} \ldots \frac{\mathrm{A}_{m-1}}{\mathrm{A}_{m-2}} \,.\, e_1^{\int_{\mathrm{T}_{m-1}}^{\mathrm{T}_m} \frac{\phi}{k\mathrm{T}^2}\,d\mathrm{T}}$$

$$\nu = \nu_{m,\,m+1} = \mathrm{A} \,.\, \frac{\mathrm{A}_1}{\mathrm{A}} \ldots \frac{\mathrm{A}_{m-1}}{\mathrm{A}_{m-2}} \,.\, \frac{\mathrm{A}_m}{\mathrm{A}_{m-1}},$$

and

$$\frac{\mathrm{A}_m}{\mathrm{A}_{m-1}} = \frac{\nu_{m,m+1}}{\nu_{mm}} \,.\, e_1^{\int_{\mathrm{T}_{m-1}}^{\mathrm{T}_m} \frac{\phi}{k\mathrm{T}^2}\,d\mathrm{T}} = \frac{p'_m}{p_m} \,.\, e_1^{\int_{\mathrm{T}_{m-1}}^{\mathrm{T}_m} \frac{\phi}{k\mathrm{T}^2}\,d\mathrm{T}}.$$

By these substitutions the general formula (17) becomes

$$\nu = \mathrm{A} \,.\, \frac{p'_1}{p_1} \,.\, \frac{p'_2}{p_2} \ldots \frac{p'_m}{p_m} \,.\, e_1^{\int_0^{\mathrm{T}'_1} + \int_{\mathrm{T}'_1}^{\mathrm{T}'_2} + \ldots + \int_{\mathrm{T}'_{m-1}}^{\mathrm{T}_m} \frac{\phi}{k\mathrm{T}^2}\,d\mathrm{T}}$$

$$\times\, e_1^{\frac{\phi'_m}{k\mathrm{T}'_m} - \int_0^{\mathrm{T}_m} \frac{1}{k\mathrm{T}} \frac{d\phi}{d\mathrm{T}}\,d\mathrm{T}} \,.\, e_1^{-\frac{\phi}{k\mathrm{T}} + \int_0^{\mathrm{T}} \frac{1}{k\mathrm{T}} \frac{d\phi}{d\mathrm{T}}\,d\mathrm{T}}$$

$$= \mathrm{A} \,.\, \frac{p'_1}{p_1} \,.\, \frac{p'_2}{p_2} \ldots \frac{p'_m}{p_m} \,.\, e_1^{\frac{\delta\phi_1}{k\mathrm{T}_1} + \frac{\delta\phi_2}{k\mathrm{T}_2} + \ldots + \frac{\delta\phi_m}{k\mathrm{T}_m}} \,.\, e_1^{-\frac{\phi}{k\mathrm{T}} + \int_0^{\mathrm{T}} \frac{1}{k\mathrm{T}} \frac{d\phi}{d\mathrm{T}}\,d\mathrm{T}}, \tag{18}$$

where $\delta\phi_1$, etc., are the jumps in ϕ_1, etc., at the various transition points. Since $p = \nu k\mathrm{T}$ we have

$$p = \mathrm{A}k \frac{p'_1}{p_1} \frac{p'_2}{p_2} \ldots \frac{p'_m}{p_m} \,.\, e_1^{\frac{\delta\phi_1}{k\mathrm{T}_1} + \frac{\delta\phi_2}{k\mathrm{T}_2} + \ldots + \frac{\delta\phi_m}{k\mathrm{T}_m}} \,.\, \mathrm{T} \,.\, e_1^{-\frac{\phi}{k\mathrm{T}} + \int_0^{\mathrm{T}} \frac{1}{k\mathrm{T}} \frac{d\phi}{d\mathrm{T}}\,d\mathrm{T}}. \tag{20}$$

By equating the right-hand sides of (13) and (20), taking logarithms and differentiating by T we get

$$\phi = w - \mathrm{T}\frac{dw}{d\mathrm{T}} + \frac{k}{\gamma - 1}\mathrm{T} - e\sigma\mathrm{T}, \tag{21}$$

or, if $\phi \equiv w$,

$$\frac{dw}{d\mathrm{T}} = \frac{k}{\gamma - 1} - e\sigma. \tag{22}$$

The validity of (21) or (22) is thus seen to be independent of the existence or otherwise of transition points.

The equations (13) and (20) apply to every phase, but the factors which do not involve T are different for the different phases. Thus in equation (13) a factor $e_1^{-\frac{eP_t}{kT_t}}$ and in equation (20) a factor $(p'_t/p_t)\,e_1^{\frac{\delta\phi_t}{kT_t}}$ is suppressed at each transition point as we cross it from the high to the low temperature side. If we divide (21) by $k\mathrm{T}^2$ and integrate with respect to T we find

$$\log \mathrm{T} - \phi/k\mathrm{T} + \int_0^{\mathrm{T}} \frac{1}{k\mathrm{T}} \frac{d\phi}{d\mathrm{T}}\,d\mathrm{T} = \frac{\gamma}{\gamma - 1} \log \mathrm{T} - w/k\mathrm{T} - e\int_0^{\mathrm{T}} \frac{\sigma}{k\mathrm{T}}\,d\mathrm{T} + \mathrm{C}_3, \tag{23}$$

where C_3 is a constant independent of T, which, however, may have different values in the different phases on account of the discontinuities at the transition points. A consideration of the values of the quantities on the two sides of any transition point shows that the jumps in C_3 are given by

$$kT_t\delta C_3 = \delta w_t - \delta\phi_t. \tag{19}$$

It follows that if w and ϕ are identical, C_3 will have the same value in all phases. In this case a comparison of (13), (20) and (23) shows that

$$\frac{\delta\phi_t}{kT_t} + \log\frac{p'_t}{p_t} = -\frac{eP_t}{kT_t} \tag{24}$$

From (1) and (2) we have

$$\frac{w'_t - w_t}{kT_t} + \log\frac{p'_t}{p_t} = -\frac{eP_t}{kT_t}. \tag{25}$$

These are identical if $\phi \equiv w$. If this is not the case the connection between ϕ and w is given by (21) so that

$$\delta\phi_t = \delta w_t - T_t\delta\left(\frac{dw}{dT}\right)_t - eT_t\,\delta\sigma_t \tag{26}$$

at any transition point, where $\delta\,(dw/dT)_t$ denotes the jump in the temperature coefficient of w in crossing the transition point. From (25) and (26), which are independent of any assumed relation between w and ϕ

$$-\delta\phi_t = T_t\delta\left(\frac{dw}{dT}\right)_T + eT_t\delta\sigma_t + kT_t\log\frac{p'_t}{p_t} + eP_t. \tag{27}$$

If ϕ and w are identical it appears from (26) that

$$\delta\phi_t = \delta w_t \tag{28}$$

and

$$\delta\left(\frac{dw}{dT}\right)_t = -e\delta\sigma_t. \tag{28.1}$$

This result is also required by (22), which applies to this case.

It will now be useful to summarise the chief results of this investigation so far attained. It appears that thermodynamic and equilibrium considerations require the following relations, between the quantities which fundamentally underlie thermionic phenomena, to hold at any transition point between two condensed phases :—

$$\log p'_t/p_t = e\,(V_t - V'_t)/kT_t\,; \tag{1}$$

$$w'_t - w_t + e\,(V_t - V'_t) = -eP_t\,; \tag{2}$$

$$\log p'_t/p_t = -\frac{w'_t - w_t}{kT_t} - \frac{eP_t}{kT_t}\,; \tag{25}$$

$$\phi'_t - \phi_t = w'_t - w_t - T_t\left\{\left(\frac{dw}{dT}\right)'_t - \left(\frac{dw}{dT}\right)_t\right\} - eT_t\,(\sigma'_t - \sigma_t)\,; \tag{26}$$

$$= -T_t\left\{\left(\frac{dw}{dT}\right)'_t - \left(\frac{dw}{dT}\right)_t\right\} - eT_t\,(\sigma'_t - \sigma_t) + kT_t\log\frac{p'_t}{p_t} + eP_t. \tag{27}$$

Of these equations only (1), (2) and (26) are independent, the others being derived from them. These equations involve no assumptions as to the relation between φ and w. If we assume that these quantities are identical (26) breaks up into (28) and (28·1) whilst (27) reduces to (25). These relations do not prescribe any very severe restrictions as to the kind of occurrences which may take place at transition points. To the usual approximation which disregards the possible difference of electron reflection in the two phases the saturation currents are in the same ratio as the pressures p_t and p_t'. From (1) we see that if there is no change in the saturation current at a transition point there will be zero contact potential difference between the two phases. The current may be either continuous or discontinuous at a transition point, and the constants A and b in the equation

$$i = \mathrm{AT}^2 e^{-b/\mathrm{T}} \tag{29}$$

change in various ways. From equation (20) for example we see that if p (or i) remains constant on crossing a transition point A in (29) will alter by a factor $e^{(\phi_t'-\phi_t)/k\mathrm{T}_t}$, whilst b will increase by the amount $(\phi_t'-\phi_t)/k$. If p jumps A and b may change in various ways, possible cases being those in which one of the two quantities jumps and the other remains constant.

The first observations of sudden reversible changes in thermionic emission were made by H. L. Cooke and the writer* in working with osmium filaments. The fuller account of our investigations which we promised has never been published, as both the data and the material were lost when I left Princeton. Recently A. F. A. Young† has found that in the case of potassium there is no discontinuity in the value of either i, A or b at the melting point. This result requires that (*a*) the contact potential between the liquid and solid phase is zero (equation (1)) (*b*) there is no heat developed when electrons are transferred from solid to liquid across the junction between these two phases ($\mathrm{P}_t = 0$ in equation (13)) (*c*) the internal latent heat has the same value for the liquid as for the solid phase (since $\mathrm{V}_t - \mathrm{V}'_t = 0 = \mathrm{P}_t$ in equation (2)). Goetz‡ has recently announced discontinuities of various types at the melting point of copper and at the melting points and transition points of some other metals. One of these results is rather surprising on account of the high values of the constant involved. Thus from his published data I find that for solid copper the value of ϕ is equivalent to 11·8 volts. This is about twice as high as the highest value of the corresponding quantity for any metal hitherto investigated. For copper he finds the ratio $b_{\text{solid}}/b_{\text{liquid}}$ to be 4·5.*

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* Richardson and Cooke, 'Phil. Mag.,' vol. 21, p. 408 (1911).

† 'Royal Soc. Proc.,' A, vol. 104, p. 624 (1923).

‡ 'Phys. Zeits.,' 24 Jahrg., p. 389 (1923).

3. *The universal constant C_1.*

In 'Roy. Soc. Proc.,' A, vol. 91, p. 530 (1915) I stated that the constant C_1 which occurs in equation (13) and similar equations, was a universal constant and a little later I† published a proof of this statement involving certain approximations. The following argument brings out certain interesting features and follows a course at first practically identical with that of pp. 389–92 *ante*, the only alteration being that instead of a single substance in two condensed phases at temperatures above and below a transition point we now have two different solid substances at the respective temperatures T_2 and T_1, joined by an extension of both substances whose temperature varies, the temperature of the junction being T_0. To avoid the complications met with in §2, we assume that all the temperatures are below all the transition points of the respective substances. In this way we arrive at

$$w_2/T_2 - w_1/T_1 + k \log p_2/p_1 - \frac{k\gamma}{\gamma - 1} \log T_2/T_1 + e\int_{T_0}^{T_2} \frac{\sigma_2}{T}\, dT + e\int_{T_1}^{T_0} \frac{\sigma_1}{T}\, dT + \frac{eP_{12}}{T_0} = 0. \qquad (30)$$

This is the same as equation (3) but the symbols have not the same meaning, the suffixes 1 and 2 now distinguishing two different substances and T_0 being the arbitrary temperature of the junction between them instead of a transition point.

Now consider a circuit consisting only of two portions of the solids 1 and 2 joined together at each end. Let one of the junctions be maintained at T_0 and the other at the absolute zero. Next apply the equation $\int dQ/T = 0$ to the reversible heat absorption when an arbitrary number of electrons are made to travel round this circuit. We thus obtain

$$\int_0^{T_0} \frac{\sigma_2}{T} dT - \int_0^{T_0} \frac{\sigma_1}{T} dT - \frac{P_{12}}{T_0} + \left(\frac{P_{12}}{T}\right)_{T=0} = 0, \qquad (31)$$

where $(P_{12}/T)_{T=0}$ is the value of P_{12}/T at the absolute zero and is equal, subject to the reservations referred to on p. 388, to the thermoelectric power of the circuit of two metals at that temperature. Now this quantity can at most be comparable with the other three terms of equation (31), all of which are small compared with some of the terms in equation (30), for example with w_2/T_2. As a first approximation, we disregard the quantity $(P_{12}/T)_{T=0}$ after substituting the value of P_{12}/T_0 from (31) in (30). We thus obtain

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* Owing to an error this ratio is inverted in the paper.

† 'Emission of Electricity from Hot Bodies,' 1st edn., p. 42 (1916).

$$w_2/T_2 + k \log p_2 - \frac{k\gamma}{\gamma - 1} \log T_2 + e \int_0^{T_2} \frac{\sigma_2}{T} dT$$
$$= w_1/T_1 + k \log p_1 - \frac{k\gamma}{\gamma - 1} \log T_1 + e \int_0^{T_1} \frac{\sigma_1}{T} dT.$$

Each side of this equation only contains quantities which refer to a single substance and to a single temperature. It follows that

$$w/T + k \log p - \frac{k\gamma}{\gamma - 1} \log T + e \int_0^{T} \frac{\sigma}{T} dT = C_1 \qquad (32)$$

has the same value for all temperatures and substances. We have only proved the invariance of C_1 to be exact with regard to temperature.

We have neglected the small term $(P_{12}/T)_{T=0}$ which has a value independent of the temperature, but which might make C_1 vary a little from one substance to another. I believe, however, that $(P_{12}/T)_{T=0}$ is not merely small, but is actually zero, for the following reasons :—

1. According to experiments of Kamerlingh Onnes and Holst quoted by Keesom* the thermoelectric powers of pairs of various metals fall away rapidly as the absolute zero is approached.
2. Calculations by Keesom* and by the writer† make $P_{12} \propto T^4$ and $\sigma \propto T^3$ as T approaches zero.
3. According to Nernst‡, his heat theorem leads to the conclusion that the thermoelectric power at very low temperatures must become infinitely small of the same order as the specific heat.
4. If P_{12}/T does not vanish at $T = 0$ negative temperatures become possible.§ It also becomes possible to diminish the entropy of part of a system by a finite amount from the value which it previously had when in equilibrium at the absolute zero, and this can be effected by the transference of an infinitesimal quantity of heat.

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* 'Communications of the Physical Laboratory Leiden,' Supplement No. 30 to Nos. 133-144, p. 24 (1913).

† 'Phil. Mag.,' vol. 28, p. 639 (1914).

‡ 'Nernst, Theoretische Chemie,' 7te Aufl., Stuttgart, p. 753 (1913).

§ Richardson, 'Phil. Mag.,' vol. 28, p. 641 (1914). I do not now think that this state of affairs would necessarily contravene the first and second laws of thermodynamics, as seems to be implied by a statement there made.

I do not feel convinced that any of these reasons taken alone is sufficient to prove that $(P_{12}/T)_{T=0} = 0$ as a logical necessity, but I think that, taken together, they establish it as a practical certainty.

The argument that C_1 is a universal constant is restricted to metallic substances which conduct electricity at $T = 0$. For other substances the left-hand side of (32) is still invariant in T, but it is difficult to know what to do with $(P_{12}/T)_{T=0}$ by this method, if the circuits do not conduct electricity at the absolute zero.

4. *On metallic conductors.*

There is a widespread impression that somehow or other the facts of thermionic electron emission favour the kinetic electron theory of metallic conduction. This is probably attributable to the fact that experiments confirm the requirement of that theory that the emitted electrons should have a Maxwell distribution of kinetic energy. Classical dynamics require this to be true for electrons in any part of the system in thermal equilibrium, and as it is found to be true for the external electrons, the only part of the system accessible to experimental examination, there is a presumption that it will also be true of the internal electrons. But this presumption has no validity apart from classical dynamics, and such properties of metals as their specific heats, their optical properties and supra-conductivity compel us to deny the adequacy of the classical dynamics as an explanation of their properties.

Until quite recently the facts of thermionic emission do not seem to me to have favoured one type of theory of metallic conduction rather than another. Recently a very accurate comparison has been made by Davisson and Germer* of the latent heat of electron emission, as measured by the cooling effect,† with the corresponding quantity deduced from the temperature emission formula, at different temperatures, using the same tungsten filament. I believe that these experiments are definitely against the kinetic theory of metallic conductors and in favour of a type of theory which makes the kinetic energy of the internal electrons either zero or at any rate practically independent of temperature. Davisson and Germer have expressed tentatively a similar conclusion, but as the matter has important bearings on what follows I prefer to re-argue it from my own standpoint.

From (13), or similar formulæ, applied below every transition point, and neglecting effects due to differences in electron reflection with temperature or with the substance, after substituting the kinetic theory formulæ

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* 'Phys. Rev.,' vol. 20, p. 300 (1922).

† Richardson and Cooke, 'Phil. Mag.,' vol. 20, p. 173 (1910).

$$p = \nu k\mathrm{T}, \tag{33}$$

$$i = \nu e\sqrt{\frac{k\mathrm{T}}{2\pi m}}, \tag{34}$$

and

$$\gamma = 5/3, \tag{35}$$

which apply to the external electrons, we obtain

$$i = \mathrm{C}_2\mathrm{T}^2 e^{-\frac{w}{k\mathrm{T}} - \int_0^{\mathrm{T}} \frac{\sigma}{k\mathrm{T}} d\mathrm{T}} \tag{36}$$

where i is the saturation current per unit area, C_2 (subject to the considerations in § 3 *ante*) is a universal constant, and w is the internal latent heat of evaporation (per electron) at temperature T. This and the remaining symbols have been defined already. The integral in (36) is small and unimportant at the present stage of accuracy of the subject; w is not a constant but may vary with T.

Now the relation between the cooling effect and the internal latent heat of evaporation may be different on different views of the behaviour of electrons in metals. Let L denote the cooling effect, ξ the difference in potential energy of an electron inside and outside the metal and η the mean kinetic energy of an internal electron, of the class which is capable of escaping, all in the same units as w. Then

$$\mathrm{L} = 2k\mathrm{T} + \xi - f(\eta). \tag{36.1}$$

where $2k\mathrm{T}$ is the average energy (kinetic) of the electrons getting away from the surface under these conditions and $f(\eta)$ denotes the average kinetic energy of an electron flowing in the stream inside the metal. $f(\eta)$ depends both on η and on the law of force for the internal collisions. On the classical theory $\eta = \frac{3}{2}k\mathrm{T}$ and

$\mathrm{L} = 2k\mathrm{T} + \xi - 2k\mathrm{T} = \xi$ assuming hard spheres,
$= 2k\mathrm{T} + \xi - 3k\mathrm{T} = \xi - k\mathrm{T}$,, inverse third power,
$= 2k\mathrm{T} + \xi - 4k\mathrm{T} = \xi - 2k\mathrm{T}$,, ,, square.

On the non-classical type of theory η is independent of T either exactly or approximately, so that for these theories we can put $f(\eta) =$ a constant c and

$$\mathrm{L} = 2k\mathrm{T} + \xi - c.$$

The internal latent heat of evaporation is the difference in the internal and external energies under equilibrium conditions. Thus :—

$$w = \tfrac{3}{2}k\mathrm{T} + \xi - \eta. \tag{36.2}$$

On the classical theory $\eta = \frac{3}{2}k\mathrm{T}$ and on the other type of theory it is a constant $= c_1$. Thus

On the classical theory :—

$$\mathrm{L} = w \quad \text{assuming elastic spheres} \tag{37}$$

$$= w - k\mathrm{T} \quad \text{,, inverse third power} \tag{38}$$

$$= w - 2k\mathrm{T} \quad \text{,, inverse square} \tag{39}$$

On the other type of theory :—

$$\mathrm{L} = w + \tfrac{1}{2}k\mathrm{T} - c + c_1.$$

As regards c and c_1 we should expect them to be equal either for $\eta = 0$ or for η constant over a predominating proportion of the displaceable electrons or for the case in which the rate of transference is unaffected by η. This seems to cover all the likely types of theory, even those which postulate Bohr orbits for the undisturbed electrons. For example, the electrons might slip from one Bohr orbit to another in a neighbouring atom, or the Bohr orbits of neighbouring atoms might intersect or coalesce at certain points, enabling the electrons to move through the material in tracks like a snake.* Thus for any likely non-classical type of theory we anticipate that

$$\mathrm{L} = w + \tfrac{1}{2}k\mathrm{T}. \tag{40}$$

In reducing their emission data Davisson and Germer use the formula $i = \mathrm{AT}^{\frac{1}{2}}e^{-b/\mathrm{T}}$. The quantity corresponding to b for the AT^2 formula (36) is obtained by subtracting† $\frac{3}{2}\mathrm{T}$ from this ; so that the quantity they measure by the emission data should be

$$kb = w + \tfrac{3}{2}k\mathrm{T}. \tag{41}$$

By comparing this equation with (37)—(40) it appears that on any view of metallic conduction which seems at all probable kb should be greater than L, but they find it to be less. The error here lies in the assumption that the quantity w in (41) really is the internal latent heat ; as it is in the preceding equations.

In the equation (36), which is valid on any theory, w represents the internal latent heat. From equation (36·2) we see that on the classical theory $w = \xi$, and on the non-classical theories $w = \xi - c_1 + \frac{3}{2}k\mathrm{T}$. By the assumptions underlying the theories c_1 can be treated as independent of T. We cannot

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[* *Note added March 8th*, 1924.—I suggest that a metal is a structure in which adjacent atoms possess Bohr orbits which have common tangents at the absolute zero thus enabling the transference of electrons through the material without loss of energy. I hope to develop this theme later.]

† 'Emission of Electricity from Hot Bodies,' 2nd edn., p. 64.

be certain about ξ but it probably also has this property. At any rate it may perhaps not be inadmissible to assign this property to it for the purpose of a model whose only function is to distinguish between the way the symbols operate in the formulæ on the different theories. By making these substitutions in (36) we find, for the temperature emission formulæ :—

(*a*) On the classical theory

$$i = C_2 T^2 e_1^{-\frac{\xi}{kT} - e\int_0^T \frac{\sigma}{kT}\,dT}.$$

On this theory the quantity b, which Davisson and Germer, using the $AT^{\frac{1}{2}}$ formula, operate in, is given by

$$kb = \xi + \tfrac{3}{2}kT = w + \tfrac{3}{2}kT,$$

and on the same theory

$L = w$ or $w - kT$ or $w - 2kT$ according to the various assumptions as to the nature of the collisions which underly equations (37)—(39).

(*b*) On the non-classical theories

$$i = C_2\, e_1^{-3/2}\, T^2 e_1^{-\frac{\xi - c_1}{kT} - e\int_0^T \frac{\sigma}{kT}\,dT}.$$

On these theories the quantity b deduced from the $AT^{\frac{1}{2}}$ formula is given by

$$kb = \xi - c_1 + \tfrac{3}{2}kT = w$$

and on the same theories

$$L = w + \tfrac{1}{2}kT - c + c_1 \qquad (42)$$

$$= w + \tfrac{1}{2}kT, \text{ in all probability.}$$

In the formula for L on the classical theory the general expression is $L = w + 2kT - \dfrac{2n}{n-1}\,kT$, where n represents the index in the assumed law* of force r^{-n}. Except for central forces for which n lies between $+1/5$ and $-1/3$, values for which the physical problem offers no excuse, L is always less than kb on the classical theory and is appreciably less on any assumed law of force for which any physical justification could be given. On the other hand the non-classical theories make L greater than kb as Davisson and Germer find. In fact, the difference between L and kb given by their experiments is equivalent to 0·132 volt which is equal, when expressed in the same units, to $\tfrac{1}{2}kT$ within the limits of accuracy of the experiments.

Thus these experiments appear definitely to be in favour of the type of theory which makes the kinetic energy of the conducting electrons in metals independent of temperature as opposed to the requirements of the classical theory.

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* Bohr, 'Phil. Mag.,' vol. 22, p. 984 (1912).

In reaching this conclusion it will be observed that no use has been made of any assumptions or conclusions about the way the actual thermodynamic quantities such as w depend on the temperature. This aspect of the matter will be dealt with in the next section.

5. *The temperature variation of w and associated questions.*

We have seen that the equation

$$\phi = w - \mathrm{T}\frac{dw}{d\mathrm{T}} + \frac{k}{\gamma - 1}\mathrm{T} - e\sigma\mathrm{T}, \tag{21}$$

where ϕ is the latent heat which enters into equation (15), is true generally of every substance in any of its condensed states. If we assume that the difference between ϕ and w is zero or negligible, we obtain an equation which I have frequently made use of, namely

$$\frac{dw}{d\mathrm{T}} = \frac{k}{\gamma - 1} - e\sigma. \tag{22}$$

This equation has met with considerable opposition. Thus, Schottky* refers to it as obviously impossible, in fact, his exact words are as follows :—"Diese Gleichung ist nun offenbar unmöglich ; und zwar nicht sowohl wegen eines Verstosses gegen die experimentellen Ergebnisse (wegen $e\sigma << \frac{3}{2}k$ müsste $\frac{dw}{d\mathrm{T}} \sim \frac{3}{2}k$ werden, wofür keinerlei Belege vorliegen), sondern einfach aus logischen Gründen. . . ." Furthermore, P. W. Bridgman† criticises me severely for disregarding the difference $\phi - w$, which he identifies as a surface latent heat. For example, he says :—"The neglect of the surface heat in Richardson's equation would therefore seem to be indefensible, and until the order of the effect is known, we cannot tell whether Richardson's equation is even approximately correct." Long before these criticisms appeared I had in mind a possible difference between ϕ and w, but I have not written about it, principally because the old evidence‡ showed that equation (22), in spite of the statements quoted above, was quite near the mark, and indeed probably near enough for many formulæ dealing with thermionic questions.

The accurate experiments of Davisson and Germer on the cooling effect, already referred to, admit of the discussion of the bearing of the experimental evidence on these points being carried to a higher degree of accuracy. We have seen that a comparative interpretation of the results on the basis of the classical and of the non-classical theories requires the rejection of the former and the adoption of the latter with the result that the cooling effect

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* 'Ber. Deutsch. Physik. Ges.,' Jahrg. 17, p. 111 (1915).

† 'Phys. Rev.,' vol. 14, p. 335 (1919).

‡ See, for example, Cooke and Richardson on the cooling effect, 'Phil. Mag.,' vol. 25, p. 642 (1913).

$$L = w + \tfrac{1}{2}kT. \qquad (40)$$

We put $c = c_1$ in (42) on the ground that the experiments show that $L = kb + \frac{1}{2}kT$ within the limits of experimental error. In (22) we may neglect $e\sigma$ compared with $k/(\gamma - 1)$ and putting $\gamma = \frac{5}{3}$ we have, if $w = w_0$ at the absolute zero,

$$w = w_0 + \tfrac{3}{2}kT.$$

This requires from (40)

$$L = w_0 + 2kT. \qquad (43)$$

L has been measured by Davisson and Germer over a range from about 2070° K. to 2310° K. for tungsten filaments. Over this range L increases by about 2 per cent., and they consider that the best line to represent their observations, if all are included and treated as of equal value, would be

$$L = \text{constant} + 3kT. \qquad (44)$$

They point out, however, that this result is largely dependent on the value of L found at the highest temperature which they have reason to believe too high, and on the values at the lower temperatures where the measured values are subject to very considerable errors on account of the smallness of the effects. When allowance is made for these facts they conclude that the results cannot be regarded as definitely contravening the formula

$$L = \text{const.} + \tfrac{3}{2}kT$$

which they are discussing. (43) would, of course, represent a line intermediate in slope between that given by this equation and (44), and careful consideration of their results and of what they say about them leads to the conclusion that they are entirely harmonious with (43), and that (44) may be taken as representing an extreme estimate of the maximum variation of L with T which could be assumed without coming into definite conflict with the experimental evidence.

Now (43) is a direct and immediate consequence of (22), so that we may conclude in the first place that the equation

$$\frac{dw}{dT} = \frac{k}{\gamma - 1} - e\sigma = \tfrac{3}{2}k,$$

approximately, represents the temperature coefficient of w to the degree of accuracy with which it has up to the present been possible to measure it. We may safely conclude that dw/dT cannot exceed $\frac{3}{2}k$ without coming into definite conflict with the experimental data. This, of course, still allows a very considerable percentage uncertainty in dw/dT itself; but this is because dw/dT is a small quantity compared with w. There is no room for any considerable variation of w with T.

We can now express quantitatively what we are disregarding by assuming $\phi \equiv w$ in (21). Without this assumption the value of $w - \phi$ is from (21)

$$w - \phi = T \cdot \frac{dw}{dT} - \frac{k}{\gamma - 1} T + e\sigma T.$$

We have seen that the value of the right-hand side of this which best fits the experimental data is zero, thus making w and ϕ identical. In any event the right-hand side cannot exceed kT without coming into conflict with the experimental evidence. Putting in the numerical values we find for this upper limit in the case of tungsten at 2300° K.,

$$w - \phi \ngtr 0{\cdot}23 \text{ volts}.$$

The value of w itself is about 4·9 volts. We therefore conclude that whilst the experimental data are in agreement with the result of assuming that ϕ and w are the same, they cannot be said definitely to exclude the possibility that there may be a small difference between these quantities which increases with rising temperature, and which in the case of tungsten at 2300° K. may approach to about 5 per cent. of w.

Gaseous Combustion at High Pressures. Part IV.—The Influence of Varying Initial Pressures upon the Rate of Pressure Development and the Activation of Nitrogen in Carbon Monoxide-Air Explosions.

By WILLIAM A. BONE, D.Sc., Ph.D., F.R.S., D. M. NEWITT, B.Sc., D.I.C., and D. T. A. TOWNEND, B.Sc., D.I.C. (Salters' Research Fellow).

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Introduction.

In the previous paper of this series* it was shown :—

(1) that when nitrogen is added as a diluent to a mixture of $2CO+O_2$ undergoing combustion in a bomb at an initial pressure of 50 atmospheres, it exerts a peculiar energy-absorbing influence upon the system, far beyond that of other diatomic gases, or of argon ;

(2) that by virtue of such influence, it retards the attainment of maximum pressure in a much greater degree than can be accounted for on the supposition of its acting merely as a diatomic diluent ;

(3) that the energy so absorbed by the nitrogen during the combustion period, which extends right up to the attainment of maximum pressure, is slowly liberated thereafter as the system cools down ; and that consequently the rate of cooling is greatly retarded for a considerable time interval after the attainment of maximum pressure ;

(4) that there is no such energy-absorbing effect (*i.e.*, other than a purely "diluent" one) when nitrogen is present in a $2H_2+O_2$ mixture similarly undergoing combustion ; but that, on the contrary, the presence of hydrogen in a CO-air mixture undergoing combustion at such high pressures so strongly counteracts the said "energy-absorbing" influence of the nitrogen, that it must be excluded as far as possible from the system before any large nitrogen-effect can be observed.

These facts were explained on the supposition that there is some constitutional correspondence between CO and N_2 molecules (whose densities are identical) whereby the vibrational energy (radiation) emitted when the one burns is of such a quality as can be readily absorbed by the other, the two thus acting in resonance. It was further supposed that, in consequence of such resonance, nitrogen becomes chemically "activated" when present during the combustion of carbon monoxide at such high pressures; and in conformity with this supposition, it was shown that such "activated" nitrogen is able to combine with oxygen more readily than does nitrogen which has merely been raised to a correspondingly high temperature in a hydrogen-air explosion.

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* 'Roy. Soc. Proc.,' A, vol. 103, p. 205 (1923).

Up to the time of publishing our previous paper we had not varied the initial pressure (usually 50 atmospheres) at which our CO-air and other explosive mixtures were fired in the bomb; and consequently we were unable to discuss the influence of initial pressure upon the phenomena associated with the explosions, and more particularly upon the "activation" of nitrogen. Thanks, however, to further timely aid from the Government Grant Committee of the Society, we were able to have constructed for us a modified form of our Petavel manometer, specially designed for experiments at initial pressures between 3 and 30 atmospheres; and as our former manometer could be employed at any initial pressure between 30 and 100 atmospheres, we have thus been able to carry out a systematic research upon the influence of varying initial pressures between 3 and 100 atmospheres upon the phenomena under discussion, the results of which are embodied in the present paper.

Shortly after the publication of our previous paper, the results of the research up to that date gave rise to some discussion* upon whether or not our results can be explained on the supposition of a purely thermal formation of nitric oxide during the CO-air explosions, without having to invoke any prior "activation" of the nitrogen. We therefore now propose to show that such suggestion is incapable of explaining the facts observed by us, and that our own view is to be preferred.

It may be recalled that our explanation of the matter was in the main supported by Dr. Fr. Hausser,† whose experiments upon the technical production of nitric oxide in coal gas-air mixtures and other similar explosions are well known. He cited some of his former tests in which CO-air mixtures, fired at 19° C. and an initial pressure of about 3·5 atmospheres, and developing a maximum pressure of about 22·35 atmospheres (equivalent to a temperature of 1867° C.), had yielded as much as 0·8 per cent. of nitric oxide in the cooled products, compared with only 0·37 per cent. as calculated from Nernst's thermodynamical equation, on the assumption that its formation is purely a thermal effect. Such tests (he said) had shown that "the formation of nitrogen oxides was between 25 and 100 per cent. greater than in the case of coal gas-air mixtures, and this in spite of the fact that the relevant conditions, viz., explosion pressures, explosion temperature and nitrogen content were practically identical, and that the difference in the oxygen content was insufficient to explain the considerable difference in the formation of the nitrogen oxides which resulted."

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* *Vide* 'Chemistry and Industry,' 23rd May and 8th June, 1923.

† *Ibid.*, 3rd August, 1923, p. 750.

He therefore considered that his own experiments had not only satisfactorily confirmed our conclusion in regard to the differences in the influence of hydrogen and carbon monoxide upon the combustion of nitrogen and shown "the possibility of nitric oxide formation by rays of short wave-length," but also that our supposition as to the formation of "activated" nitrogen may be correct. It should be noted that, whereas Hausser seems more inclined to regard "the known action of ultra-violet rays which undoubtedly occur when gaseous mixtures are exploded" as the prime cause of the nitric oxide formation in his experiments, we consider that our results can best be explained on the supposition of a primary "activation" of the nitrogen molecule by its absorption of the peculiar vibrational energy (radiation) emitted by carbon monoxide burning at high pressures. It will, however, be shown later how the results of our further experiments described herein raise doubts as to whether the initial pressure (3·5 atmospheres) at which Hausser fired the CO-air mixtures in his said experiments was sufficiently high to allow of his obtaining any "activation" of nitrogen in the sense implied and realised in ours.

Criteria of the Activation of Nitrogen in our High Pressure Experiments.

Seeing that the supposition of the "activation" of nitrogen by its absorbing the radiation emitted by the burning carbon monoxide in our high pressure explosions has evoked some discussion, it seems desirable to call attention to the criteria of its occurrence under such conditions, in order that the true interpretation of our pressure-time curves may be better understood.

In general, when a gaseous mixture is exploded in our bomb apparatus the greater part k of the energy Σ so liberated rapidly appears as increased kinetic energy of the gaseous system as a whole, and causes the observed rise in pressure. A small part r appears in a radiant form, which in ordinary circumstances traverses the gaseous medium without sensible loss and, being absorbed by the walls of the vessel, has no effect upon the observed maximum pressure. In such a case (*e.g.*, with either a hydrogen-air or an undiluted carbon monoxide oxygen explosion) the pressure-time curves show no exceptional feature; for on ignition the pressure rises very rapidly to the maximum, after which the normal cooling period immediately sets in unretarded by any appreciable exothermic effect. Such normal cooling curves have certain characteristic features, which are easily recognised by anyone familiar with them, and cannot be mistaken.

Supposing, however, that in a CO-air explosion at high initial pressure, nitrogen can intercept and absorb the peculiar radiation emitted by the burning carbon monoxide, thereby acquiring increased internal (*i.e.*, vibrational) energy, and becoming chemically more active than normal nitrogen molecules of the same mean kinetic energy. Then the maximum pressure attained in the explosion would be unaffected by such absorption, except in so far as any time-lag in the pressure development caused by it might involve some extra cooling effect by the walls of the explosion chamber during the actual combustion period, for which a proper cooling "correction" can usually be applied. The "corrected" maximum pressure would not be affected by any radiation absorbed by the nitrogen during the explosion.

When, however, during the subsequent cooling period, the "activated" nitrogen molecules slowly revert to the normal condition, the radiant energy absorbed by them during the explosion would be degraded and reappear in a kinetic form, *i.e.*, as heat. In other words, the normal cooling of the gaseous medium would be sensibly retarded by an exothermic effect caused by the said energy degradation, and consequently the resulting "cooling-curve" would be abnormal in character. Such would be the course of events whenever the experimental conditions do not permit of any appreciable secondary oxidation of the "activated" nitrogen to nitric oxide during the "explosion period," and the criteria of nitrogen-activation would be an undiminished "corrected" maximum pressure, followed by a marked exothermic effect during the subsequent cooling-period, *e.g.*, when compared with the corresponding data for an isothermic CO-oxygen mixture* at the same initial pressure.

In cases where the experimental conditions permit (as they undoubtedly sometimes do) of the secondary oxidation during the combustion period of part of the "activated" nitrogen primarily produced, some of the kinetic as well as of the radiant energy developed during the explosion would be absorbed, with consequent lowering of the "corrected" maximum pressure.

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* The expression "isothermic" mixture is used throughout this paper as implying such as not only develop on explosion the same total energy but whose combustion products as a whole ordinarily have the same volumetric heat capacities; thus $2CO + O_2 + 4N_2$, $2CO + O_2 + 4O_2$, & $2CO + O_2 + 4CO$, or indeed any CO-air mixture in which the nitrogen is wholly or partly replaced by its equivalent of either O_2 or CO would be isothermic in such sense.

And inasmuch as part of the nitric oxide so formed would probably be decomposed during the earlier part of the subsequent cooling period, more particularly until the temperature had fallen to about 2000° C., below which further decomposition would be unlikely, there would probably also be a considerable exothermic effect observable during such earlier part of the cooling period. Therefore, the criteria of some secondary formation of nitric oxide from the " activated " nitrogen primarily produced during the explosion period would be a lowered " corrected " maximum pressure followed by an abnormally slow " cooling period," *e.g.*, when compared with the behaviour of an isothermic CO-oxygen mixture exploded at the same initial pressure.

From the foregoing, it follows that whenever an analysis of the pressure-time curve in a particular $CO—O_2—N_2$ explosion shows *either* (a) a marked exothermic effect during, say, the first second of the " cooling period," without any appreciable lowering of the " corrected " maximum pressure, *or* (b) that the magnitude of the said exothermic effect is several times greater than the diminution in the " corrected " maximum pressure, as compared with the behaviour of the corresponding isothermic CO-oxygen mixture in like circumstances, the primary cause concerned must be the " activation " of the nitrogen itself rather than any secondary formation of nitric oxide. And it was the constant occurrence of such results in our previous experiments, when various $CO—O_2—N_2$ mixtures were exploded at an initial pressure of 50 atmospheres, that caused us to discard the idea of a primary NO-formation in favour of the N_2-activation theory.

To illustrate this point, which indeed is crucial as between the two views, we have reproduced in Table I the results of an analysis of the pressure-time records obtained in typical experiments in which isothermic mixtures $2CO+O_2+4R$ (where $R = N_2$, O_2 or CO) were exploded in our bomb apparatus at initial pressures of 50 atmospheres. Attention is specially directed to the following considerations :—

(1) In the first two experiments (Nos. 9 and 15), where no more than a negligible amount of adventitious nitrogen was present, but the $2CO+O_2$ " knall gas " was diluted with either $4O_2$ or 4CO respectively, the whole course of events was quite normal, and, as might be expected, the "corrected " maximum pressures, as well as the observed pressure-falls during the first second after t_m, were practically identical.

(2) In the next two experiments (Nos. 11 and 13), where N_2 was present, but an excess of CO made the conditions highly unfavourable to any secondary NO-formation, there were marked exothermic effects (proportional to the

relative N_2 concentrations) during the first second of the cooling period, without any material lowering of the "corrected" maximum pressure, as compared with the corresponding results for Nos. 9 and 15 with the isothermic N_2-free mixtures. The evidence of N_2-activation, in the sense implied by us, is here conclusive.

Table I.—Analyses of Experimental Results with Isothermic Mixtures all fired at an Initial Pressure of 50 Atmospheres.

Experiment No.	9	15	11	13	3	6	7
$2CO + O_2$ "knall-gas" diluted with :—	$4O_2$	$4CO$	$CO + 3N_2$	$2CO + 2N_2$	$4N_2$	$O_2 + 3N_2$	$2O_2 + 2N_2$
t_m secs.	0·005	0·010	0·115	0·065	0·190	0·065	0·035
P_m obs.	460	450	426	430	409	422	424
P_m corrd.	460	455	455	450	440	435	430
P. fall in 1 sec. after t_m (atmos.)	200	197	131	150	93	102	124
P. equivalent of exothermic effect during 1 sec. after t_m (atmos.)	nil.	nil.	40	22	67	70	54
Ditto $\div N_2$....	nil.	nil.	13	11	15·75	23·3	27
T_m abs.	2680°	2615°	2470°	2495°	2380°	2450°	2475°
Remarks	Normal results when N_2 is absent P_m. corrd. =455 to 460. No exothermic effect during cooling period.		Primary activation of N_2 but no secondary NO formation. P_m corrd. = 450 to 455. Marked exothermic effect during cooling period.		Primary N_2—activation *plus* some secondary NO formation P_m corrd. = 430 to 440. Large exothermic effect during cooling period.		

Note.—t_m = time (in secs.) required for the attainment of the maximum pressure P_m, and the value P_m corrd. was obtained by applying an appropriate cooling correction to the observed P_m value.

(3) In the fifth experiment (No. 3) a normal CO-air mixture ($2CO + O_2 + 4N_2$) was exploded; here the conditions apparently allowed some secondary NO-formation during the explosion period from the "activated" nitrogen primarily produced, because there was an appreciable lowering of the "corrected" maximum pressure (as compared with Nos. 9 and 15), amounting to some 15 or 20 atmospheres. But the magnitude of the observed exothermic effect during the first second of the subsequent cooling period was no less than 67 atmospheres,

or nearly four times as great, a circumstance which again proves conclusively the primary N_2-activation.

(4) Finally, in the two last experiments (Nos. 6 and 7), where excess of oxygen was present, and the conditions (especially in No. 7) were highly favourable to a secondary NO-formation, there was a lowering of between 20 and 30 atmospheres in the "corrected" maximum pressure (as compared with those in Experiments 9 and 15), indicative of increasing NO-formation during the explosion period. But the corresponding exothermic effects observed during the first second of the subsequent cooling period were as much as 70 and 54 atmospheres respectively.

Indeed, when rightly viewed, the results of these seven typical experiments prove that whenever N_2 was originally present, its "activation" by the radiation from the burning CO was precedent to any subsequent NO-formation, which latter only occurred as a secondary effect when the experimental conditions were favourable.

The Hygroscopic Condition of the Gaseous Mixtures Exploded.

The bomb and its accessory appliances, as well as our experimental method were fully described on pp. 206 to 209 of our previous paper (*loc. cit.*), to which the reader is referred. It may be added that the purified (undried) gases used in making the explosive mixtures were always separately passed slowly into the bomb from their respective storage cylinders through a special drying tube containing an 8-inch length of re-distilled phosphoric anhydride, so that the gaseous mixtures would always be exploded in the same state of comparative (though not absolute) dryness, the explosion chamber having previously been dried out by means of a current of hot dry air.

In this connection it may be recalled how some of our earlier experiments have proved that, at such high initial pressures as are usually employed by us, water vapour has a very much smaller influence upon the combustion of carbon monoxide than at atmospheric pressure. This point was fully dealt with in a paper recently published elsewhere by us,* *à propos* of two papers bearing upon it by H. B. Dixon and N. S. Walls and W. Payman and R. V. Wheeler.† We were unable to detect any appreciable differences between the t_m's in comparative experiments at 50 atmospheres initial pressure with normal CO-air mixtures in which the gases *either* (*a*) had been stored for some weeks previously in cylinders containing redistilled phosphoric anhydride, and the bomb itself had been thoroughly dried out in a current of hot dry air, and the explosion chamber had been kept evacuated in contact with redistilled phosphoric anhydride for at least three or four days immediately preceding each experiment, *or* (*b*) were slowly introduced undried into the bomb from their respective storage cylinders through a tube packed with wetted glass wool. In both cases $t_m = 0{\cdot}18$ sec. In a third series of experiments, in which the hygroscopic conditions were intermediate between (*a*) and (*b*), t_m was reduced to 0·15 sec. Such results suggest the possibility of carbon monoxide being able to combine directly with oxygen at high initial pressures; but this is a matter needing further experimental study before a definite decision can be arrived at.

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* 'Trans. Chem. Soc.,' vol. 123, pp. 2008–2021 (1923).

† *Ibid.*, pp. 1025 and 1251.

The Influence of Varying Initial Pressure upon the Explosion of a Normal Hydrogen-Air Mixture.

Before proceeding to discuss the influence of initial pressure upon the "activation" of nitrogen in the expolsion of CO-air mixtures, it seems desirable to show how the explosion of a normal hydrogen-air mixture ($2H_2+O_2+4N_2$), where no appreciable activation of nitrogen occurs, is affected by the initial pressure in our bomb apparatus. Accordingly in Table II are summarised the results of a series of experiments over a wide range of initial pressures between 3 and 75 atmospheres.

In this and all the following tables included in the paper :—

P_i = the initial pressure in atmospheres at which the mixture was fired.

P_m obs. = the observed maximum pressure in atmospheres attained in the explosion.

P_m corrd. = the said maximum pressure "corrected" for any cooling during the actual explosion period, whenever the experimental data enabled it to be estimated.

t_m = the time in seconds taken for the attainment of maximum pressure.

T_m abs. = the approximate maximum temperature (abs.) attained in the explosion, assuming the chemical contraction to have been completed by t_m.*

It will be seen that in all cases the pressure rose with extreme rapidity to its maximum, which was always attained within 0·005 sec. Our recording apparatus

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* It may be remarked that this assumption accords very well with the internal evidence of our experiments as a whole, and it has therefore been adopted throughout this paper.

Table II.—Showing Influence of Varying Initial Pressure upon the Explosion of a Normal Hydrogen-Air ($2H_2 + O_2 + 4N_2$) Mixture.

Experiment No.	30	31	32	33	34
P_i	3	10	25	50	75
t_m	0·005	0·005	0·005	0·005	0·005
P_m obs.	23	78	200	403	635
P. in 1 sec. after t_m.	5	23	76	178	315
P. fall in 1 sec. after t_m.	18	55	124	225	320
Percentage fall in ditto	78·3	70·5	62·0	55·8	50·3
Ratio P_m/P_i.	7·7	7·8	8·0	8·1	8·5
T. abs. at which mixture was fired	292°	293°	292°	290°	289°
$T_{max.}$ (abs.)	2620°	2665°	2720°	2740°	2820°

does not at present allow of our measuring such small time intervals with greater accuracy, although we are fairly sure that t_m tended to become shorter as the initial pressure increased. Also, owing to the shortness of t_m, it is impossible to apply any "cooling correction" to the observed values of P_m; but in any case it would presumably be very small. It will be seen that the ratio P_m/P_i increased slightly (from 7·7 to 8·1) with the initial pressure up to 50 atmospheres; from which also it would seem as though t_m was actually decreasing as the initial pressure rose. At an initial pressure of 75 atmospheres the ratio P_m/P_i became 8·5, but the explosion was so violent that possibly the spring of our Petavel gauge may have been momentarily overstretched a little. On the assumption that the chemical contraction was completed at P_m, the approximate maximum temperature reached in these explosions would vary between 2620° and 2820° abs.

The pressure-time records obtained were so nearly alike in type, when the respective (P_m—P_i) values were each plotted to the same length on the P-ordinate, that it will suffice for purposes of illustration if we reproduce in fig. 1, A and B, the records obtained in the two extreme experiments; as might be expected, the only noticeable difference between them is in the respective rates of cooling after t_m.

Perhaps the most important feature of the pressure-time records, however, is that immediately upon the attainment of P_m, the curve always turned sharply and at once assumed the character of a cooling curve unretarded by any exothermic process. There was never any sign of "after burning," nor yet of any nitrogen "activation." Also, it is evident that, although the maximum temperatures reached in three of these experiments exceeded 2700° abs., no

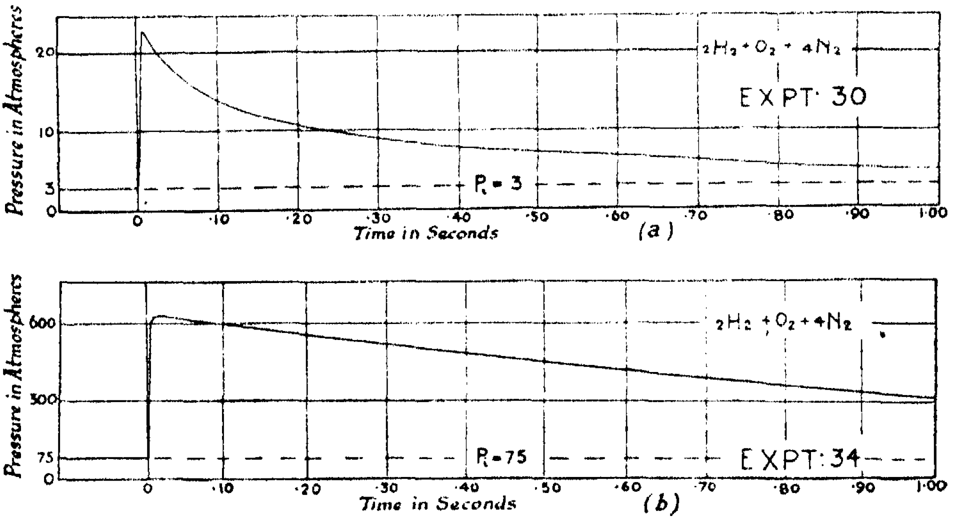

FIG. 1.

had appreciable nitric oxide formation occurred up to t_m, or otherwise its subsequent partial decomposition would presumably have had some discernible retarding influence upon the earlier portion of the cooling period, which, in fact, was never manifest.

The Influence of Varying Initial Pressures upon the Explosion of (a) undiluted $2CO+O_2$ Knall-gas and (b) the same diluted with Argon.

(*a*) That the effects of progressively increasing the initial pressure in the explosion of an undiluted mixture of carbon monoxide and oxygen in their combining ratio were to shorten t_m and to increase the ratio P_m/P_i, is proved by the results (summarised in Table III) of the following typical series of experiments in which initial pressures of 4·3, 21·4 and 50 atmospheres were employed. The pressure-time curves for the first and third experiments of this series are reproduced in fig. 2 (A and B).

Attention is directed to the great rapidity of the explosions at the two higher pressures, which is comparable with that observed in the case of the hydrogen-air explosions; also to the circumstance that in no case could any "after-burning" be detected after t_m. Indeed, these experiments seem inconsistent with the view that the maximum pressure attained on explosion is materially affected by the dissociation of carbon dioxide. It will also be seen that the maximum temperature attained in the third experiment of the series (P_i = 50 atmospheres) was about 5280° abs.

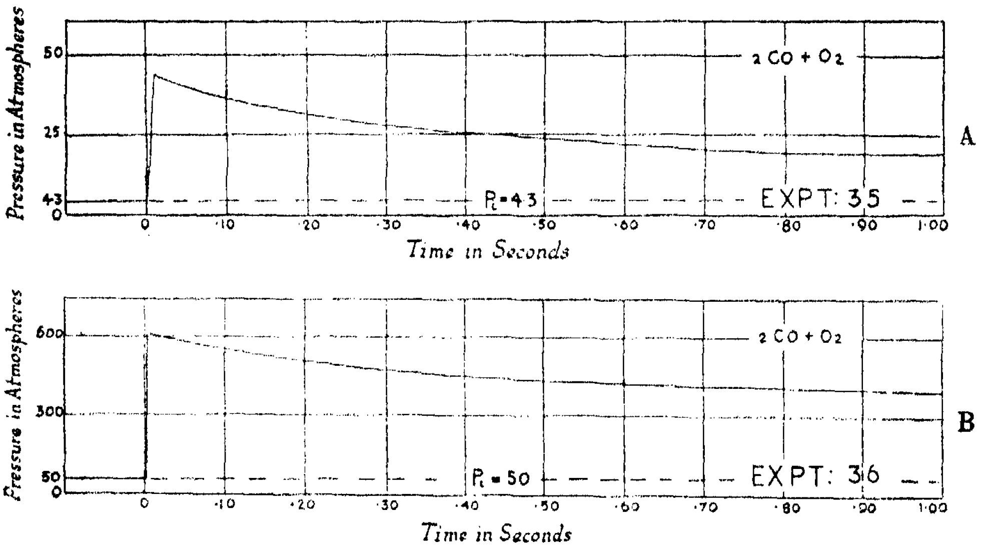

FIG. 2.

Table III.

Experiment No.	P_i	t_m	P_m obs.	P_m/P_i.	P. in 1 sec. after t_m.	P. fall in 1 sec. after t_m.		T_m abs.
						Atms.	Per Cent.	
35	4·3	0·0125	43·0	10·0	19	24	55·8	4360°
22	21·4	0·005	245·0	11·5	152	93	38·0	5120°
36	50·0	0·005	605·0	12·1	387	218	36·0	5280°

(*b*) In Table IV are similarly shown the effects of varying initial pressure upon the explosion of the theoretical $2CO+O_2$ mixture diluted with as much of the monatomic inert argon as would make it correspond with a normal CO-air mixture in which nitrogen is wholly replaced by argon. The initial pressures successively employed were 3, 10, 50 and 75 atmospheres, and the results should be compared with those detailed later on for the corresponding series of experiments with the normal CO-air mixture. It will be seen that, with the exception of the first increase in P_i from 3 to 10 atmospheres, which slightly lengthened t_m, all subsequent increases progressively shortened it; also that the ratio P_m/P_i uniformly increased with P_i.

Table IV.—Results obtained with $2CO + O_2 + 4Ar$ Mixtures.

Experiment No.	37	38	21	39
P_i (atmos.)	3	10	50	75
t_m (secs.)	0·035	0·050	0·025	0·015
P_m obs. (atmos.)	25·5	89	510	780
P_m corrd. (atmos.)	26·0	92	516	785
P. in 1 sec. after t_m	9·7	45	306	522
P. fall in 1 sec. after t_m	15·8	44	204	258
Percentage ditto	62·0	49·6	40·0	32·7
Ratio P_m/P_i	8·5	8·9	10·2	10·4
T_i abs.	293°	291°	290°	281°
T_m abs.	2910°	3030°	3460°	3420°

The four pressure-time curves obtained are reproduced in fig. 3, from which it will be seen that only in the experiment at the lowest initial pressure (3 atmospheres) was there any sign of an exothermic effect after P_m had been reached. It would seem as though in this particular case there had been perhaps a slight "after-burning" due to the combustion not having been quite completed on the attainment of P_m. This is probably the reason why the effect of the first increase in P_i (from 3 to 10 atmospheres) was to lengthen the observed t_m; for the time required *to complete the combustion* was probably actually longer at 3 than at 10 atmospheres. In all the other experiments at high pressures there was no sign of any exothermic effect after P_m had been attained.

The ratio P_m/P_i progressively increased from 8·5 to 10·4 as the initial pressure was raised from 3 to 75 atmospheres. And on the assumption that the "chemical contraction" in respect of the gas burnt had been completed by t_m, these ratios would correspond with maximum temperatures of 2910° and 3420° abs. respectively.

These experiments, therefore, may be regarded as proving that the effect of increasing the initial pressure in the explosion of either (*a*) an undiluted $2\,CO+O_2$ "knall-gas" or (*b*) the same diluted with the inert monatomic argon, is to shorten the time required for the attainment of maximum pressure, as well as to increase the observed ratio P_m/P_i. Also they serve to show how very small is the mere "statistical" influence of a diluent upon such explosions.

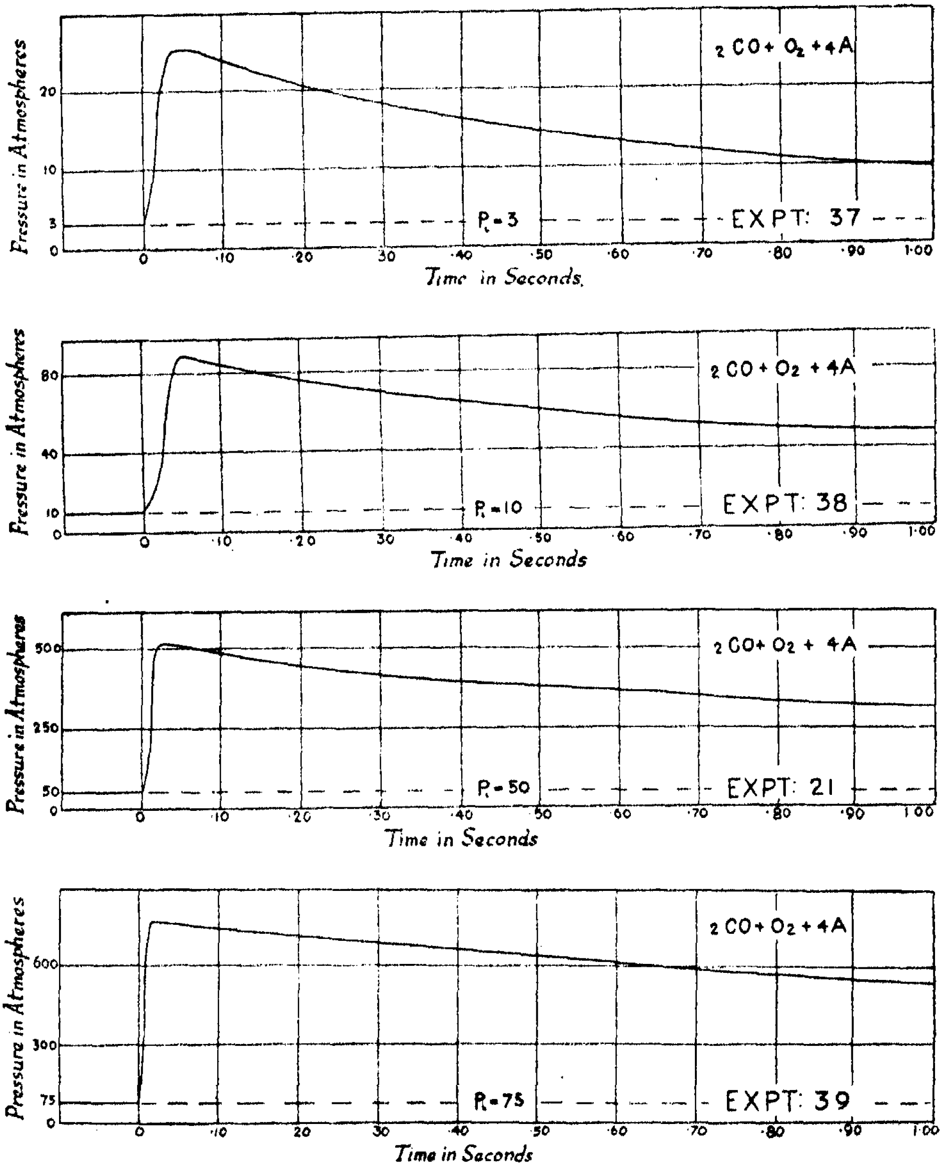

FIG. 3.

The Influence of Varying Initial Pressure upon the Activation of Nitrogen by the Radiation from burning Carbon Monoxide.

If, as we suppose, nitrogen can intercept and absorb the radiation emitted by burning carbon monoxide, with consequent increase in its own vibrational energy, it might be anticipated that the phenomenon would be influenced considerably by the degree of initial compression under which the $CO+O_2+N_2$ mixtures are exploded. For the greater the density of the nitrogen in the explosion chamber, the greater would be the chance of its intercepting the radiation in question. Indeed, it might also be expected that there would be some limiting compression below which the phenomenon would hardly be discernible; and that the more the initial compression is increased above such limit the greater would be the resulting effect. The following experiments will show how completely such anticipations have been fulfilled.

In these experiments normal carbon monoxide-air mixtures $(2CO+O_2+4N_2)$ were successively fired in the bomb at initial pressures of 3, 10, 25, 50, 75 and 100 atmospheres respectively, and the resulting pressure-time records carefully analysed. And, for comparative purposes, a parallel series of experiments was also carried out with an isothermic $2CO+O_2+4O_2$ mixture at corresponding

Table V.—Experimental Results with $2CO + O_2 + 4N_2$ and $2CO + O_2 + 4O_2$ Mixtures at Varying Initial Pressures.

P_i (atmos.)	3		10		25		50		75		100
Experiment No.	40	41	42	43	44	45	3	9	46	47	48
$2CO+O_2$ diluted with	$4N_2$	$4O_2$	$4N_2$	$4O_2$	$4N_2$	$4O_2$	$4N_2$	$4O_2$	$4N_2$	$4O_2$	$4N_2$
t_m (secs.) ...	0·07	0·06	0·10	0·045	0·15	0·01	0·19	0·005	0·30	0·005	0·45
P_m obs. ...	21·4	22·8	75	77	193	215	409	460	635	760	880
P_m corrd. ...	23·4	24·1	80	80	209	215	440	460	682	760	—
Diffs. P_m corrd. $4O_2$ & $4N_2$	negligible		nil.		6·0		20·0		78·0		—
P. in 1 sec. after t_m	8·9	9·9	42·5	33·5	133	115	316	260	510	500	—
P. fall in 1 sec. after t_m	12·5	12·9	32·5	43·5	60	100	93	200	125	257	—
% fall in 1 sec. after t	58.4	56.2	42.5	56.5	31.1	46.5	22.75	43.5	19.7	33.8	—
P. equiv. of exothermic effect in 1 sec.	nil.	nil.	10	nil.	17	nil.	64	nil.	40 to 50	—	—
Ratio P_m/P_i	7·13	7·6	7·5	7·7	7·7	8·6	8·2	9·2	8·5	10·1	8·8
T_i abs. ...	293°	293°	293°	292°	291°	292°	291°	291°	289°	290°	290°
T_m abs. ...	2435°	2600°	2565°	2625°	2615°	2930°	2785°	3120°	2832°	3412°	2975°

initial pressures, except at 100 atmospheres where it was feared that the violence of the explosion might be too much for the strength of the bomb.

In order to bring out as clearly as possible the true significance of these important results, we have tabulated them (Table V) in adjacent vertical columns for each of the two isothermic mixtures, $2CO+O_2+4N_2$ and $2CO+O_2+4O_2$, respectively, at each of the successive initial pressures. And, from what has been said in the earlier part of the paper, the following criteria will apply, namely:—(1) the non-occurrence of "nitrogen activation" in any particular experiment with the CO-air mixture will be shown by a very close approximation between the t_m, the "corrected" P_m, and the rate of pressure-fall after t_m, respectively, for that experiment and the corresponding values found for the $2CO+O_2+4O_2$ mixture at the same initial pressure; (2) a primary "activation" of nitrogen without any secondary NO-formation in any CO-air experiment will be shown by a longer t_m, and a much slower rate of cooling

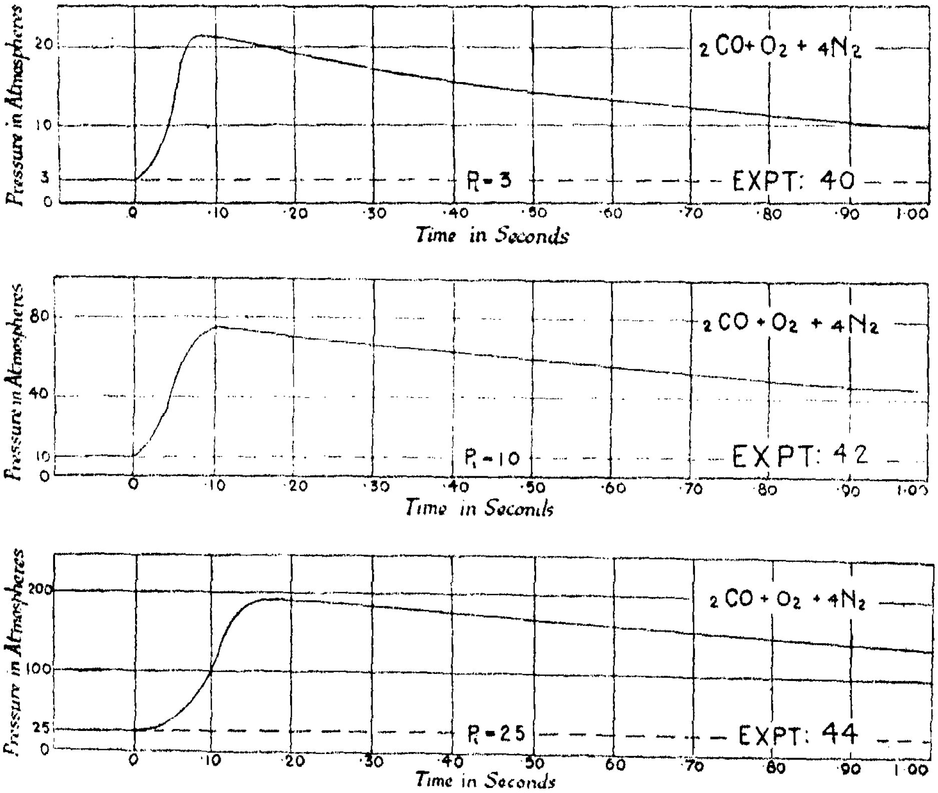

FIG. 4.

thereafter, together with practically the same "corrected" P_m values, as compared with those obtained in the corresponding $2CO+O_2+4O_2$ experiment at the same initial pressure; whilst (3) a secondary formation of nitric oxide superposed upon a primary N_2-activation in a CO-air experiment will be shown by a decidedly lower "corrected" P_m, as well as by a longer t_m, and a much slower rate of cooling thereafter, than in the corresponding $2CO+O_2+4O_2$ experiment at the same initial pressure. In figs. 4 and 5 are reproduced all the pressure-time records for the $2CO+O_2+4N_2$ and the $2CO+O_2+4O_2$ series respectively, and it is important that they should be carefully compared. The curves are analysed in Table V.

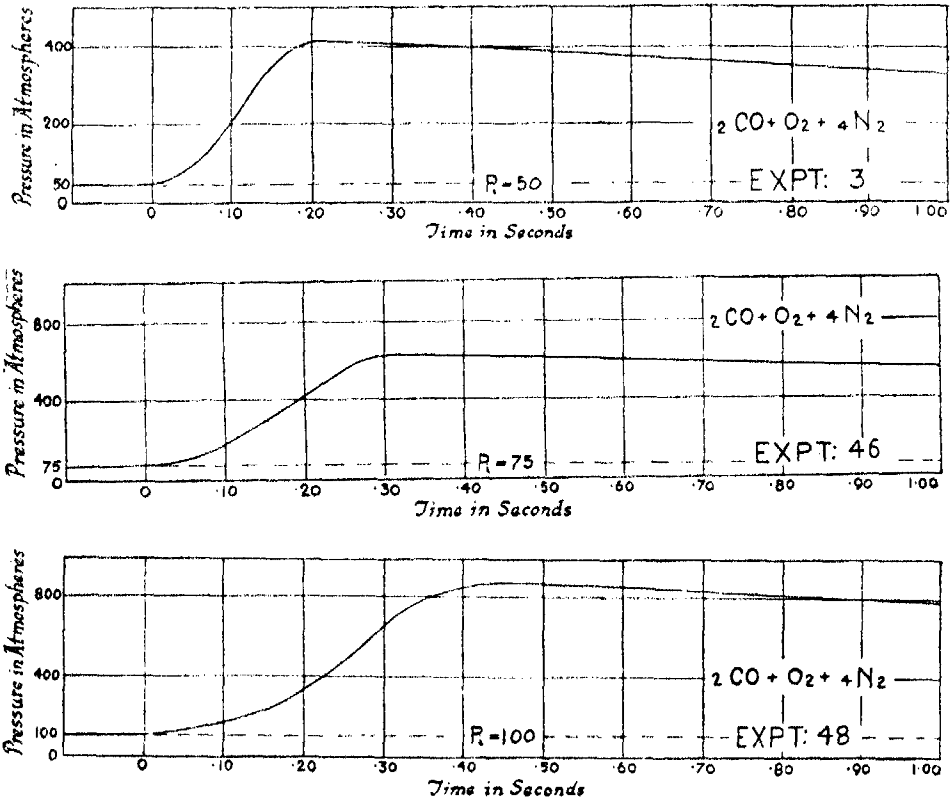

FIG. 4 (*continued*).

The outstanding general feature of the results is that, whereas in the $2CO+O_2+4O_2$ series t_m progressively diminished with increasing initial pressure (thus agreeing well with the corresponding observations with the $2H_2+O_2+4N_2$ and $2CO+O_2+4Ar$ mixtures), in the $2CO+O_2+4N_2$ series it increased with

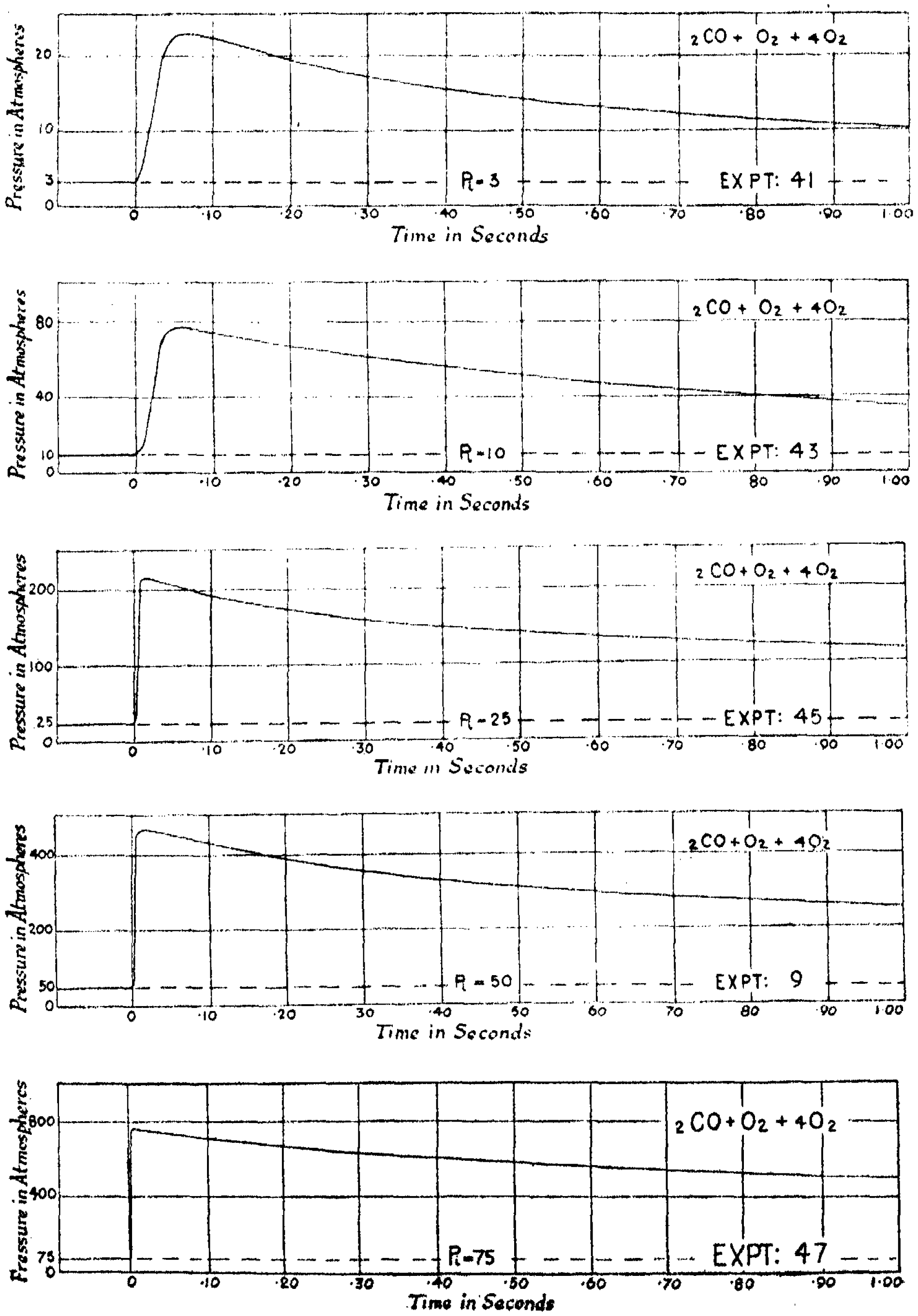
Pressure in Atmospheres
20
10
3
0
$2CO + O_2 + 4O_2$
R = 3
EXPT: 41
0
·10
·20
·30
·40
·50
·60
·70
·80
·90
1·00
Time in Seconds
Pressure in Atmospheres
80
40
10
0
$2CO + O_2 + 4O_2$
R = 10
EXPT: 43
Time in Seconds
Pressure in Atmospheres
200
100
25
0
$2CO + O_2 + 4O_2$
R = 25
EXPT: 45
Time in Seconds
Pressure in Atmospheres
400
200
50
0
$2CO + O_2 + 4O_2$
R = 50
EXPT: 9
Time in Seconds
Pressure in Atmospheres
800
400
75
0
$2CO + O_2 + 4O_2$
R = 75
EXPT: 47
Time in Seconds

FIG. 5.

the initial pressure, *e.g.*, from 0·07 seconds at 3 atmospheres to 0·19 seconds at 50 atmospheres, and to no less than 0·45 seconds at 100 atmospheres, with corresponding intermediate values. All this is entirely conformable with our theory of nitrogen activation in such cases.

Table VI.—Analyses of Pressure-Time Curves obtained with $2CO + O_2 + 4N_2$ and $2CO + O_2 + 4O_2$ Mixtures at Varying Initial Pressures.

P_i (atmos.)	3		10		25		50		75		100
Experiment No.	40	41	42	43	44	45	3	9	46	47	48
$2CO + O_2$ diluted with	$4N_2$	$4O_2$	$4N_2$	$4O_2$	$4N_2$	$4O_2$	$4N_2$	$4O_2$	$4N_2$	$4O_2$	$4N_2$
Time in seconds.	Pressures in Atmospheres.										
0·000....	3	3	10	10	25	25	50	50	75	75	100
0·005....	—	—	—	—	—	—	—	400*	—	760*	—
0·010....	—	—	—	—	—	215*	—	—	—	—	—
0·045....	—	—	—	77*	—	—	—	—	—	—	—
0·050....	15	22·6	45	77	48	201	110	433	105	732	120
0·060....	—	22·8*	—	—	—	—	—	—	—	—	—
0·070....	21·4*	—	—	—	—	—	—	—	—	—	—
0·100....	21·2	22·3	75*	75	105	187	206	412	175	700	170
0·150....	20·3	21·0	73	71	191	182....	350	393	275	680	250
0·155....	—	—	—	—	193*	—	—	—	—	—	—
0·190....	—	—	—	—	—	—	409*	—	—	—	—
0·200....	19·0	19·5	71	67	191	177	409	376	420	665	370
0·250....	17·9	18·4	69	64	188	170	408	360	585	650	490
0·300....	16·9	17·3	67	62	183	160	402	350	635*	636	650
0·400....	15·3	15·6	63	57	179	151	390	330	626	610	870
0·450....	—	—	—	—	—	—	—	—	—	—	880*
0·500....	14·0	14·4	58·5	52	169	142	380	311	608	590	880
0·600....	13·0	13·4	55·5	48	161	135	370	299	602	563	865
0·700....	11·9	12·5	53	44	154	131	361	287	585	551	850
0·800....	11·0	11·5	50	41	147	127	352	276	569	538	820
0·900....	10·3	10·8	46·5	38	143	124	343	268	557	524	800
1·000....	9·5	10·3	44·5	35	139	120	334	259	545	503	780
Percentage fall in 1 sec. after t_m	58·4	56·2	42·5	56·5	31·1	46·5	22·75	43·5	19·7	34·2	—

* Denotes attainment of maximum pressure.

Turning now to the individual experiments it will be seen that:—

(1) *With $P_i = 3$ atmospheres,* the practical identity between the t_m's, P_m's (corr.), and the rates of pressure fall after t_m, in the two corresponding $2CO+O_2+4N_2$ and $2CO+O_2+4O_2$ experiments is a sure sign that no appreciable

N_2-activation had occurred in the CO-air experiment. This is why it may be doubted whether Dr. F. Hausser obtained any N_2-activation in our sense in the CO-air experiments cited by him (*loc. cit.*) where the initial pressure was only 3·5 atmospheres.

(2) *With* $P_i = 10$ *atmospheres*, there was unmistakable evidence of some incipient N_2-activation in the CO-air experiment; for in addition to t_m having been prolonged to 0·10 sec., there was also a decided retardation of the rate of cooling after t_m as compared with the corresponding $2CO+O_2+4O_2$ experiment, without there being any appreciable difference between the "corrected" P_m values in the two cases. Undoubtedly, therefore, the primary N_2-activation had not been accompanied by any appreciable secondary NO-formation.

(3) *With* $P_i = 25$ *atmospheres*, the primary N_2-activation in the CO-air experiment was still more marked than in (2), and it was now apparently associated with some incipient secondary NO-formation.

(4) *With* $P_i = 50$ *atmospheres*, the primary N_2-activation in the CO-air experiment had considerably increased, and was again associated with some secondary NO-formation.

(5) *With* $P_i = 75$ *or* 100 *atmospheres*, it is evident that the primary N_2-activation in the CO-air experiment had now become so intense as to produce a considerable secondary NO-formation in the flame.

In fig. 6 are plotted, all to the same scale, the portions of each cooling curve for 1 second after the attainment of P_m, for both the $2CO+O_2+4N_2$ and the $2CO+O_2+4O_2$ series respectively. With $P_i = 3$ atmospheres, the two curves are indistinguishable, showing that in the CO-air explosion the nitrogen had acted merely as a diatomic diluent. With $P_i = 10$ atmospheres, there is a quite discernible difference between them, showing an incipient N_2-activation in the CO-air explosion. At higher pressures the difference becomes more and more marked as the pressure rises.

It is important to note that in each of the two CO-air explosions when $P_i = 25$ or 50 atmospheres, the magnitude of the exothermic effect observed during the first second of the "cooling period" after t_m exceeded by almost three times the amount by which the "corrected" P_m was diminished during the actual explosion period, as compared with the corresponding $2CO+O_2+4O_2$ experiments. This we regard as conclusive evidence of a primary N_2-activation having preceded any secondary NO-formation in the explosions.

From the results taken as a whole, we conclude that in the explosion of a normal CO-air (*i.e.*, $2CO+O_2+4N_2$) mixture :—

(1) There is a certain limiting initial pressure, somewhere between 3 and 10 atmospheres and probably nearer the latter, below which no appreciable activation of the nitrogen occurs, it acting merely as a diatomic diluent.

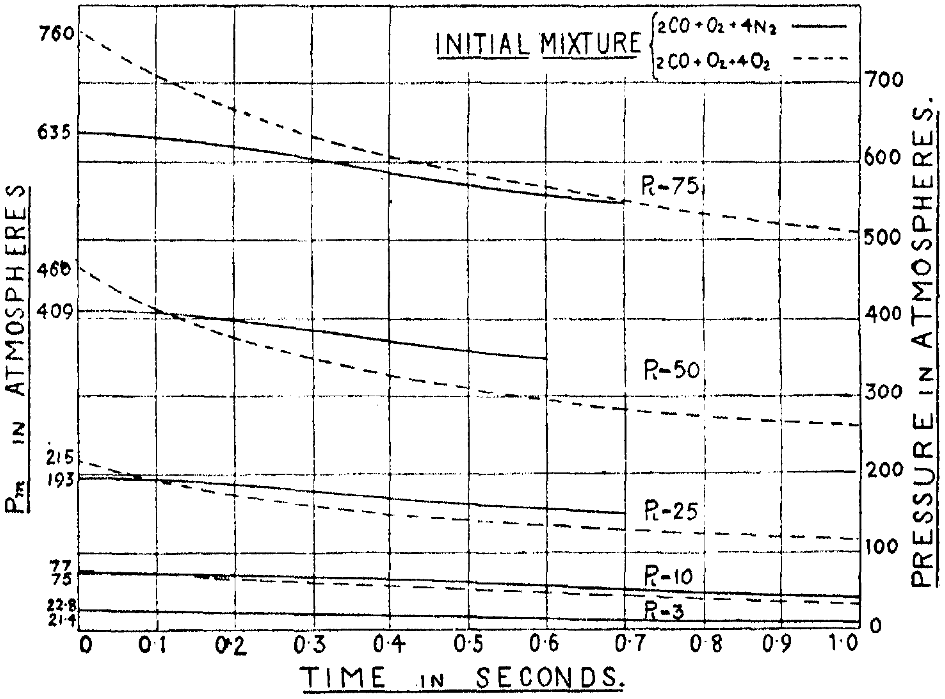

FIG. 6.

(2) Activation of the nitrogen is just discernible at an initial pressure of 10 atmospheres, but is at first unassociated with any appreciable secondary NO-formation.

(3) The primary N_2-activation increases with the initial pressure and is eventually (at about 25 atmospheres) followed by a partial secondary NO-formation.

(4) With an initial pressure of 75 atmospheres or higher, the primary N_2-activation becomes so intense that it is followed almost instantaneously by a large secondary NO-formation during the combustion period.

Experiments with Various Mixtures $2CO+O_2+4R$ (*where* R = *diluent*) *at an Initial Pressure of* 75 *Atmospheres.*

In view of the intensity of the nitrogen-activation observed when a normal CO-air mixture was exploded at an initial pressure of 75 atmospheres (*vide* the preceding section), it was decided to make a further comparative series of experiments at the said initial pressure, but employing mixtures in which the nitrogen of the normal CO-air mixture was progressively replaced by equivalent volumes of other diluents (O_2, CO or Ar).

The results of these experiments, which are summarised in Table VII, generally support the previous conclusion that at such high pressures the primary N_2-activation is immediately followed by a considerable secondary NO-formation, except where the original mixtures contain a fairly large excess of carbon monoxide, *e.g.*, in the case of $2CO+O_2+2CO+2N_2$ mixtures.

Table VII.—Experimental Results with Various $2CO + O_2 + 4R$ Mixtures at an Initial Pressure of 75 Atmospheres.

Experiment No.	$2CO+O_2$ Knallgas diluted with	T_i abs.	t_m.	P_m		P_m/P_i	P. fall in 1 sec. after t_m		T_m abs.
				obs.	corrd.		Atmos.	Per Cent.	
46	$+4N_2$	289°	0·30	635	682	8·5	131	20	2865°
49	$+O_2+3N_2$	289°	0·10	658	672	8·8	155	23·5	2965°
50	$+2O_2+2N_2$	288°	0·03	675	680	9·0	165	25·0	3020°
47	$+4O_2$	283°	0·005	760	760	10·1	257	33·8	3345°
51	$+CO+3N_2$	289°	0·135	680	700	9·1	161	23·7	3070°
52	$+2CO+2N_2$	289°	0·100	701	720	9·4	179	25·5	3170°
53	$+4CO$	287°	0·015	720	727	9·6	223	30·9	3215°
54	$+Ar+3N_2$	278°	0·240	680	717	9·1	150	22·1	2950°
55	$+2Ar+2N_2$	285°	0·130	725	744	9·7	163	23·0	3225°
39	$+4Ar$	284°	0·015	780	780	10·7	258	32·7	3545°

It will be observed that, in the last named-case, the pressure equivalent of the exothermic effect observed during the first second of the cooling period after t_m (32 atmospheres) exceeded by more than four times the amount (7 atmospheres) by which the "corrected" P_m value fell below that for the corresponding isothermic $2CO+O_2+4CO$ mixture, which again is a sure sign of a primary N_2-activation having occurred in the particular explosion referred to.

The Secondary Formation of Nitric Oxide in our Experiments.

Although reference was made in our previous paper to the fact that there was always a much greater oxidation of nitrogen in our CO-air than in our H_2-air explosions at initial pressures of 50 atmospheres, the point was not further elaborated. But its obvious theoretical interest, as well as its bearing upon the important problem of nitrogen fixation, impels us to make some further observations upon it.

The possibility of successfully effecting a large scale fixation of nitrogen by its direct oxidation has already been sufficiently demonstrated in the well-known arc process and by explosion methods, and is occupying many minds. The difficulties connected therewith arise from the facts (*a*) that nitric oxide is an endothermic compound, the formation of whose gram molecule from its elements involves an absorption of 21·6 K.C.Us.; (*b*) that, although obtainable by the reversible reaction $N_2 + O_2 \rightleftharpoons 2NO$, it is not rapidly so formed at temperatures below 2000° abs., and it readily decomposes at temperatures above 2500° abs., and (*c*) that the proportion of it in equilibrium with its elements between 2500° and 3000° abs., even in the most favourable circumstances, does not exceed between 2 and 3 per cent. Thus, for example, according to Nernst and his co-workers,* the thermal equilibrium for the NO-air system at various temperatures is as follows :—

T. abs.	Percentages of N_2	O_2	NO
1877°	78·89	20·69	0·42
2023°	—	—	0·52 to 0·80.
2580°	78·08	19·88	2·05
2675°	77·98	19·78	2·23

Moreover, the same authorities have estimated that the following times are required for the formation or decomposition of half the equilibrium proportion of nitric oxide at various temperatures.

T. abs.	Half-formation.	Half-decomposition.
1900°	2·08 minutes	16,000 minutes.
2100°	5·06 seconds	1,400 seconds.
2500°	0·01 seconds	5·6 seconds.
2900°	0·0000345 seconds	0·005 seconds.

If such estimates can be accepted as approximately reliable, it would seem (*a*) that in a gas-air explosion not much NO-formation can be expected unless the temperature attained exceeds 2500° abs., and (*b*) that but little of it would survive unless the subsequent cooling down to well below such temperature is exceedingly rapid. Now we are informed that the maximum concentration of nitric oxide in the gases from the technical electric arc process does not usually exceed 1·5 per cent., which is much below the calculated equilibrium proportion for the high temperature of the arc. Doubtless the decomposition of much of the NO actually formed in the arc is unavoidable, however rapidly the issuing gases may be cooled down. It should be mentioned that in 1907 F. Haber and A. Koenig obtained yields of nitric oxide in experiments with specially cooled high tension arcs at temperatures below the melting point of platinum, using mixtures of nitrogen and oxygen at 100 m.m. pressure, which were far higher than those calculated from Nernst's thermodynamical equation ; but they concluded that the formation of the nitric oxide in such circumstances was due to collision of electrons at comparatively low temperatures. Indeed, we believe it is now thought by many authorities that the formation of nitric oxide in the electric arc is due primarily to the establishment of an electrical equilibrium, upon which a thermal equilibrium is subsequently superposed.

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* 'Zeit. Anorg. Chem.,' vol. 45, p. 116 (1905); vol. 49, pp. 212, 229 (1906).

It is long ago since Bunsen observed the formation of oxides of nitrogen in certain circumstances during gaseous explosions ; and Hausser's recent efforts (*loc. cit.*) to establish a successful technical bomb-explosion process for the production of nitric oxide are well known. He now explodes mixtures of coke-oven gas (freed from sulphur) with excess of air (pre-heated to 300° C.) in 300 litre bombs at an initial pressure of 5 atmospheres, with rapid cooling of the resulting products, which then (he finds) contain on an average between 0·6 and 0·7 per cent. of nitric oxide.

Whilst it is impossible to make a direct determination of the amount of nitric oxide present in the products of a gaseous explosion at the moment of maximum pressure, the amount which survives in the products after they have been cooled down to the room temperature can be estimated without difficulty. And, as already indicated, the thermal decomposition $2NO = N_2 + O_2$ would be exceedingly rapid during the earlier part of the cooling period, *i.e.*, down to 2500° abs. Also, any excess of combustible gas would be inimical to the survival of nitric oxide ; on the other hand, an excess of oxygen would both help to preserve it and ensure its conversion into NO_2 at temperatures below about 900° abs.

In order, however, to gain some further general information concerning the influence of such factors as initial pressure, excess oxygen, etc., upon the secondary NO-formation in such explosions as these we are investigating, we have carried out a number of experiments in which the comparative amounts of NO and/or NO_2 surviving in the cooled products of various N_2-containing explosive mixtures, when fired in our bomb apparatus, have been determined. The principal results of these will now be briefly described.

A.—*Influence of Excess Oxygen upon NO-formation.*—We first of all exploded, at an initial pressure of 75 atmospheres, a series of isothermic mixtures in which the $2CO + O_2$ "knall-gas" was diluted with varying proportions of nitrogen and oxygen, in such wise that, beginning with a normal CO-air mixture ($2CO+O_2+4N_2$), half of its nitrogen was progressively replaced by its equivalent of oxygen, *i.e.*, until the nitrogen and excess oxygen present were in equimolecular proportions, which presumably would be the most favourable circumstances for the secondary NO-formation in the explosion. After the products had cooled down to the room temperature at the end of each experiment, the total NO and/or NO_2 remaining in the system was determined by the phenol-sulphonic acid method. The results were finally expressed in terms of the volume-percentage of nitric oxide in the gaseous products at atmospheric pressure, in Table VIII.

It will be seen that until there was a considerable excess of oxygen present in the mixture exploded, the amount of NO/NO_2 which survived in the cooled products was relatively small. In the case of $2CO+3O_2+2N_2$ mixture, however, where it amounted to as much as 3 per cent., on opening the valve of the bomb after the explosion, so that the gaseous products were released, a strong smell of NO_2 pervaded the laboratory.

Table VIII.—Experiments at an Initial Pressure of 75 Atmospheres.

Experiment No.	Mixture exploded.	t_m secs.	T_m Abs.	Time required for cooling down from T_m to 2500° abs.	Per cent. of NO in cooled Products.
56	$2CO+O_2+4N_2$	0·30	2830°	About 0·5 to 0·6 sec.	0·03
57	$2CO+1\frac{1}{2}O_2+3\frac{1}{2}N_2$	—	—		0·05
58	$2CO+2O_2+3N_2$	0·09	2950°		1·00
59	$2CO+3O_2+2N_2$	0·03	3025°		3·00

It should be noted that the maximum temperatures reached in the several explosions were all high enough to allow of the attainment, within the time-interval t_m, of the supposed thermal equilibrium proportion of nitric oxide, but that the 0·6 second occupied by the cooling down from T_m to 2500° abs. would probably be long enough to permit of the decomposition of a considerable part of any NO formed during the explosion. In the circumstance, the survival of as much as 3 per cent. of NO in Experiment 59 is perhaps remarkable, whilst the experiments as a whole constitute satisfactory evidence of the secondary

NO-formation being largely dependent upon the presence of excess oxygen in the mixture exploded.

B.—*The secondary NO-formation is not a merely thermal effect.*—The amount of NO_2 surviving in the cooled products when a mixture containing $2H_2+3O_2+2N_2$ was exploded in the bomb at an initial pressure of 75 atmospheres (Experiment No. 60) was next determined. The maximum temperature reached (in about 0·005 second) in the explosion would be about 2820° abs., whilst the time taken for the products to cool down from it to 2500° abs. was only 0·12 seconds as compared with 0·6 seconds in the corresponding $2CO+3O_2+2N_2$ experiment (No. 59). The amount of NO_2 finally found in the products (including all the liquid obtained when the bomb was thoroughly washed out with distilled water at the end of the experiment) did not exceed 0·07 per cent., or only one-thirtieth of that which survived in the corresponding experiment with carbon monoxide. We regard such a result as further supporting our view that any secondary NO-formation in our $CO-O_2-N_2$ explosions is not a merely thermal effect but really depends upon a prior N_2-activation.

C.—*Influence of Initial Pressure.*—In a final series of experiments, we compared the percentage of NO_2 surviving in the cooled products when mixtures containing $2CO+3O_2+2N_2$ (*i.e.*, the most favourable proportions of excess O_2 and N_2) were successively exploded in the bomb at initial pressures of 3, 25, 50 and 75 atmospheres, with the following results (Table IX), which can hardly mean other than that the formation of nitric oxide in the explosion of mixtures containing CO, N_2 and excess of O_2 depends in a high degree upon some factor which is controlled by the initial pressures.

Table IX.—Experiments with Mixture $2CO+3O_2+2N_2$ at Varying Initial Pressures.

Experiment No.	P_i atm.	t_m secs.	T_m abs.	Time required to cool down from T_m to 2500° (abs.) sec.	Percentage NO in cooled gaseous products.
60	3	0·065	2500°	—	0·3
61	25	0·060	2680°	0·20	0·8
62	50	0·035	2880°	0·35	1·8
59	75	0·030	3020°	0·60	3·0

Reviewing as a whole the evidence as derived from this part of our work, we are led to conclude (i) that the formation of NO in such explosions is in the main primarily due to the combustion of carbon monoxide under pressure in the presence of nitrogen and not to any purely thermal cause, (ii) that it is promoted by some factor which is controlled by the initial pressure, and (iii) that its survival largely depends upon there being an excess of ogygen in the system.

Summary and Concluding Remarks.

The additional facts established by this research may be summarised in the following numbered paragraphs :—

(1) Whereas on exploding in our bomb normal hydrogen-air ($2H_2 + O_2 + 4N_2$) mixtures, or a $2CO + O_2$ "knall-gas" (whether undiluted or diluted with excess oxygen or argon) an increase in the initial pressure shortens the time required to develop the maximum pressure, the reverse is the case with normal CO-air ($2CO + O_2 + 4N_2$) mixtures, where t_m progressively increases from 0·07 sec. when $P_i = 3$ atmospheres to as much as 0·45 sec. when it is 100 atmospheres.

(2) When $P_i = 3$ atmospheres, there is little or no difference as regards either t_m, P_m, or the subsequent rate of cooling between the behaviour of a $2CO + O_2 + 4N_2$ mixture and that of the isothermic $2CO + O_2 + 4O_2$ mixture. In other words, at such initial pressures nitrogen acts in a CO-air explosion merely as a diatomic diluent, and exerts no other appreciable energy-absorbing function, which is only manifested at higher pressures.

(3) With $P_i = 10$ atmospheres, the peculiar energy-absorbing function of nitrogen in the explosion of a normal CO-air mixture is already apparent, and thereafter increases progressively with the initial pressure, until at initial pressures of 50 atmospheres and upwards it becomes a very marked feature of the phenomena associated with the explosion.

(4) When the function in question first becomes manifest and over a considerable range of initial pressure thereafter (*e.g.*, 10 to nearly 25 atmospheres) it is marked by a large exothermic effect during the cooling period subsequent to the attainment of the maximum pressure, *without any appreciable lowering of the corrected P_m value.*

(5) Over a still higher range of initial pressure, namely from 25 to 50 atmospheres, and probably somewhat beyond, the magnitude of the exothermic effect manifested during the first second of the cooling period subsequent to the attainment of the maximum pressure exceeds by about three times any lowering of the latter.

(6) Even at 50 atmospheres initial pressure, if the experimental conditions are rendered unfavourable to NO-formation by partial replacement of the nitrogen of a normal CO-air ($2CO + O_2 + 4N_2$) mixture by its equivalent of carbon monoxide, there is again always a considerable exothermic effect observ-

able during the first second of the cooling period after the attainment of the maximum pressure on explosion, without any material diminution in the corrected P_m value.

(7) The corrected maximum pressure attained in the explosion of a normal CO-air mixture is slightly affected by secondary NO-formation at an initial pressure of 25 atmospheres, and more so at higher pressures, until at initial pressures of 75 and 100 atmospheres it is considerably so affected.

(8) Such secondary NO-formation is favourably influenced by (*a*) higher initial pressure, and (*b*) the presence of excess of oxygen in the mixture exploded; and with regard to (*b*), when $P_i = 75$ atmospheres the optimum condition seemed to be reached when *half* the nitrogen of the normal CO-air mixtures ($2CO + O_2 + 4N_2$) is replaced by its equivalent of oxygen.

(9) So far as the instruments we have employed can show, nitrogen exerts no peculiar energy-absorbing function in the explosion of normal hydrogen-air mixtures at any initial pressure up to 75 atmospheres, which is the highest we have dared to employ in our present bomb in such cases. Moreover, not only was there no time lag in the development of maximum pressure in such explosions, but also the subsequent cooling curves were unaffected by any appreciable exothermic influence.

(10) Even when a $2H_2 + 3O_2 + 2N_2$ mixture is exploded at an initial pressure of 75 atmospheres, any NO-formation is incomparably smaller than in the case of the corresponding $2CO + 3O_2 + 2N_2$ mixtures under similar circumstances, although the condition as regards total energy development and relative concentration of combustible gas, excess oxygen and nitrogen, are precisely the same, and the difference between the maximum temperatures developed in the two explosions (about 2820 and 3020° abs.) is not great.

(11) Speaking generally, no appreciable "after burning" or other exothermic effect could be detected when such mixtures as $2H_2 + O_2 + 4N_2$, $2CO + O_2$, or $2CO + O_2 + 4Ar$ were exploded at initial pressures exceeding 10 atmospheres, and there was no sign of the maximum temperature in the explosion of an undiluted $2CO + O_2$ "knall-gas" at such initial pressure being limited by the dissociation of carbon dioxide, although the maximum temperatures attained in certain cases were as high as 5200° abs.

Such being the principal facts, we think they are best explained on our supposition of a *primary* N_2-activation by absorption of the peculiar radiation emitted by burning CO molecules, which may or may not be followed by a *secondary* NO-formation, according as the experimental conditions favour the latter or not. Such a view is capable of explaining all the facts brought to light up to the present during this research, and therefore holds the field. On the other hand, the alternative explanation of a *primary* NO-formation of a *purely thermal character* seems incapable of explaining the facts referred to in the foregoing paragraphs (4), (5), (6), (9) and (11), and therefore must be discarded.

As was pointed out in our previous paper, the supposition of a resonance-action between carbon monoxide and nitrogen in CO-air explosions accords with modern views as to the similar electronic constitutions of CO and N_2 molecules; and H. Nagoka* has recently published a paper in which attention is drawn to what he considers to be an approximate coincidence between the band spectra of the two gases, a matter which at least seems worthy of further investigation. We wish it to be understood that our present view is that the particular radiation emitted by burning carbon monoxide which is effective in activating the nitrogen in our experiments arises rather from direct interactions between CO molecules and :O atoms (or possibly O_2 molecules) than from interaction between CO and OH_2 molecules; because it can be now deduced from the results published in the Bone-Haward paper (Part II hereof)† that the partial replacement of the CO by H_2 in a CO-air explosion at high initial pressures counteracts the N_2-activation, a circumstance which harmonises with the views about the mechanism of CO-combustion advanced in that paper. We believe that further light upon this aspect of the matter may be gained from a spectroscopic investigation of the effect of gradually adding hydrogen to a carbon monoxide flame; and experiments with this end in view have already been started at the Imperial College by one of us in conjunction with Prof. A. Fowler and Mr. F. R. Weston (Gas Research Fellow).

Thanks to a further generous grant from the Government Grant Committee, which we hereby gratefully acknowledge, we have been enabled to order a new explosion bomb twice as strong as the present one, with which we contemplate carrying out further experiments on similar lines to those described in this paper but at still higher initial pressures. Also, we intend studying the effects of diluting a $2CO + O_2$ "knall-gas" with helium before explosion at high pressures, as well as completing the programme of work outlined at the end of our previous paper.

In conclusion, we desire also to thank the Department of Scientific and Industrial Research for maintenance grants and the Salters' Institute of Industrial Chemistry for a Fellowship which has enabled two of us to devote the whole of our time to the investigation.

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* 'Japanese Journal of Physics,' vol. 1, p. 49 (1922).

† 'Roy. Soc. Proc.,' A, vol. 100, p. 67 (1921).

The Large-Angle Scattering of α-Particles by Light Nuclei.

By E. S. Bieler, Ph.D. (Cantab.), late Scholar of the Exhibition of 1851
for McGill University, 1923.

(Communicated by Prof. Sir E. Rutherford, F.R.S.—Received February 4, 1924.)

§ 1. The hypothesis of the nuclear structure of the atom was first put forward by Sir Ernest Rutherford* in 1911 to explain the phenomena of large-angle scattering of α-particles. It was found that when a beam of α-particles passed through matter, the number of particles scattered at large angles far exceeded the number that would be expected on probability considerations, if these large deflections were made up of a number of successive small deflections. The facts could only be explained on the assumption that these deflections were single deflections, occurring as the result of a very close encounter between the α-particle and the atom. The experimental results could be explained quantitatively on the assumption that the mass of the atom was concentrated in a nucleus of small volume at the centre, with a positive charge approximately equal numerically to half the atomic weight. The force was an inverse-square electrostatic one and the electrons outside contributed practically nothing to the scattering owing to their small mass.

The nuclear theory of the atom soon received very strong support from different sources of evidence. The extensive series of experiments carried out by Geiger and Marsden† on the scattering of α-particles by gold and silver between the angles of 5° and 150° furnished results in perfect agreement with the theory, and showed that, within the limit of experimental error, the inverse-square law held between the α-particle and the nucleus down to distances of 3×10^{-12} cm. At the same time, Bohr,‡ combining the idea of nuclear structure of the atom with the new hypothesis of stationary states, suggested by the quantum theory, showed how the simpler series spectra could be completely and accurately explained on the inverse-square law. The pioneer work of Moseley§ on X-ray spectra gave strong support to the idea first proposed by Van den Broek‖ that the nuclear charge, instead of being quite equal to one-half the atomic charge, was indeed equal to the atomic number or number of the place occupied by an element in the periodic table.

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* Rutherford, 'Phil. Mag.,' vol. 21, p. 669 (1911).

† Geiger and Marsden, 'Phil. Mag.,' vol. 25, p. 604 (1913).

‡ Bohr, 'Phil. Mag.,' vol. 26, pp. 1, 476 (1913).

§ Moseley, 'Phil. Mag.,' vol. 26, p. 1024 (1913); vol. 27, p. 703 (1914).

‖ Van den Broek, 'Phys. Zeit.,' vol. 14, p. 32 (1913).

Both the nuclear charge and the law of force in the atom have of late been determined with much greater accuracy. By an ingenious geometrical arrangement, Chadwick[*] was able to show by α-particle scattering experiments that the nuclear charge was actually equal to the atomic number, and that the law of force was the inverse square in the neighbourhood of 10^{-11} cm. from the nucleus. Hartree[†] has since shown that on the inverse-square law it is possible to build up a self-consistent system of electron orbits within the atom, using known X-ray and optical energy levels. This gives strong support to the view that the inverse-square law is also obeyed at the distances, mainly greater than 10^{-11} cm., at which these electrons revolve.

The inverse-square law has been shown to hold to 1 per cent., down to about 7×10^{-12} cm., the distance at which scattering occurred in the case of the faster α-particles investigated by Chadwick,[‡] and to continue to hold approximately down to a distance of 3×10^{-12} cm., as in Geiger and Marsden's[§] experiments. There is, however, no evidence that it holds down to nuclear dimensions. Different considerations show that it must break down somewhere.

The phenomena of radio-active decay point to the complexity of the nucleus in the case of some of the heaviest elements. The recent work of Aston[||] and other workers on positive rays shows beyond doubt that the whole-number rule is obeyed to a high degree of approximation by the atomic weight of elements, and drives one to the conclusion that the mass of all nuclei must be made up of one common unit, the hydrogen nucleus, or proton. In addition, the work of Rutherford and Chadwick,[¶] on the disintegration of atomic nuclei by α-particle impact, has shown that a particle of the charge and mass of the hydrogen nucleus can actually be driven out of the nuclei of some of the lighter atoms, and therefore that protons form an integral part of them. We may therefore take it that the nucleus of any atom contains a number of protons equal to its atomic weight, together with a number of electrons equal to the difference between the atomic weight and the atomic number.

Now, this highly complex nucleus is restricted to a very small volume. In the case of gold, it must contain 197 protons and 118 electrons, and still act approximately as a point charge at 3×10^{-12} cm. It is very difficult to see how it can be in equilibrium in such a restricted space under electrostatic forces alone. We are thus driven to expect that other forces intervene at these very short distances, forces presumably of attraction between like charges, which neutralise the electrostatic repulsion and maintain the nucleus in equilibrium. The existence of such forces has already been assumed by Rutherford* in his explanation of the driving-out of an H-particle from the nucleus by an α-particle, for he supposes that an H-particle can be moving about a nucleus as a close satellite. Only a force of attraction between it and the nucleus will allow it to do so.

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[*] Chadwick, 'Phil. Mag.,' vol. 40, p. 734 (1920).

[†] Hartree, 'Proc. Camb. Phil. Soc.,' vol. 21, p. 625 (1923).

[‡] Chadwick, *loc. cit.*

[§] Geiger and Marsden, *loc. cit.*

[||] Aston, 'Phil. Mag.,' vol. 38, p. 707 (1919), etc.

[¶] Rutherford, 'Phil. Mag.,' vol. 37, p. 537 (1919); 'Roy. Soc. Proc.,' A, vol. 97, p. 314 (1920).

Besides this indirect evidence, there is striking experimental evidence that, in one case at least, the inverse-square law breaks down at a short distance from the nucleus. It has been shown, first by Rutherford† and then by Chadwick and the author,‡ that the number of H-nuclei projected in a forward direction by α-particles far exceeds the number which can be accounted for on the inverse-square law. In order to account for the phenomenon, it is not sufficient to bring in the fact that the α-particle has a structure whose dimensions are probably comparable with the distance of closest approach of the H-nucleus, but it is necessary to assume forces of a non-electrostatic nature. Indeed, the α-particle was found to act more or less as though it were an oblate spheroid of semi-axes 4×10^{-13} cm. and 8×10^{-13} cm., travelling along its short axis. The H-nuclei would be repelled according to the inverse-square law so long as they did not come into actual contact with the spheroid, but would rebound elastically from it on actually striking it. On this view, the surface of the spheroid represents the limits of a region inside which the forces increase with great rapidity.

The object of this paper is to describe a series of experiments in which a deviation from the inverse-square law has been obtained, in the case of very close approach of the α-particles to the nuclei of aluminium and magnesium.

§ 2. *The Large-Angle Scattering by Light Nuclei.*

When an α-particle of mass M, charge E, and velocity V is deflected through an angle ϕ by a nucleus of mass m and charge Ne, the distance of closest approach on the inverse-square law is given by :—

$$D = \mu (1 + \sec \theta) \qquad (1)$$

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* Rutherford and Chadwick, 'Phil. Mag.,' vol. 42, p. 809 (1921); vol. 44, p. 417 (1922).

† Rutherford, 'Phil. Mag.,' vol. 37, p. 537 (1919).

‡ Chadwick and Bieler, 'Phil. Mag.,' vol. 42, p. 923 (1921).

where

$$\mu = \frac{N\rho E}{V^2}\left(\frac{1}{M} + \frac{1}{m}\right) \tag{2}$$

and

$$\tan\theta = \frac{m \cot\phi + \sqrt{(m^2 \operatorname{cosec}^2\phi + M^2)}}{M + m}. \tag{3}$$

For the heavier atoms whose mass m is large compared with M, this distance is approximately proportional to the atomic number N of the deflecting atom. Also, the relation between θ and the angle of deflection ϕ is practically independent of the masses. The apsidal distance for a given deflection is, therefore, approximately proportional to the atomic number of the deflecting atom.

For the lighter atoms the approximation is not so close, but we may still say that the lighter the deflecting atom, the shorter is the apsidal distance for a given angle of deflection. It is, therefore, with light atoms that there is the greatest likelihood of finding out something about the nucleus and the field of force surrounding it by means of experiments on α-particle scattering.

One of the few attempts to obtain the large-angle scattering of α-particles by light atoms was that made by Loeb,* who studied the scattering by carbon and aluminium at angles approaching 180°. Owing to the very small scattering at these large angles, he had considerable difficulty in counting, due to the large disturbing effect of a small amount of radio-active contamination. He was unable to reach any conclusion with regard to carbon, and thought he detected a slight increase over the theoretical scattering in the case of aluminium.

In the experiments about to be described, the first element tried was carbon, obtained by heating *in vacuo* small sheets of rice-paper, kept flat between mica sheets. Owing to the difficulty of completely driving out the hydrogen present, and the uncertainty of the correction to be applied for it, as well as the impurities of higher atomic number, the experiments with carbon had to be abandoned.

The two elements finally selected were aluminium, which can be obtained in the form of thin leaves, containing practically no other impurity than about 0·15 per cent. of iron,† and magnesium, which was kindly furnished by the Magnesium Company of Great Britain, in sheets thin enough to act as a scatterer.

The same arrangement of radio-active source, scattering foil and fluorescent screen was adopted as in Chadwick's‡ experiments on scattering, and in those of Chadwick and the writer* on the collision of α-particles with H-nuclei. It is shown diagrammatically in fig. 1. AA′ is a scattering foil of metal leaf in the form of an annular ring, limited inside and outside by diaphragms. R is a radio-active source and S a zinc-sulphide screen. They are placed along the axis of the scattering foil at equal distances on either side of it. It is easily seen that all the particles which strike the screen at S will have been scattered through an angle between ϕ_1 and ϕ_2.

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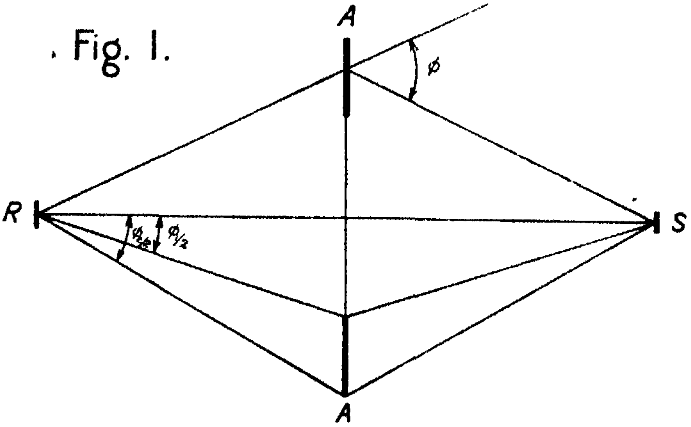
* Loeb, 'Phil. Mag.,' vol. 42, p. 819 (1921).

† The analysis was kindly carried out by Mr. C. T. Heycock, F.R.S., and Mr. F. H. Jeffery, of the Chemical Laboratory, Cambridge.

‡ Chadwick, *loc. cit.*

Fig. 1.



Chadwick has shown that, under these conditions, the number of scattered α-particles which strike the screen is given by :—

$$\nu = \frac{Qntb^2}{64\overline{r^2}}\left[\cot\phi_{1/2}\operatorname{cosec}\phi_{1/2} - \cot\phi_{2/2}\operatorname{cosec}\phi_{2/2} + \log\tan\phi_{2/4} - \log\tan\phi_{1/4}\right] \quad (1)$$

where Q = the number of α-particles emitted by the source per second,
n = the number of atoms per unit volume in the foil,
t = the thickness of the foil,
$\overline{r^2}$ = the mean square of the distance from the source to the foil, and
$b = 2NeE/MV^2$.

Here, Ne is the nuclear charge of the scattering atom, and M, V, and E are the mass, velocity, and charge of the α-particles.

The formula above is true, provided that the motion imparted to the deflecting nucleus by the α-particle can be neglected. The correction to be applied to take this into account has been worked out by Darwin.† It is easily shown that, even in the case of magnesium at an angle of 100°, the correction amounts to less than 2 per cent., diminishing to about 0·35 per cent. at 60°. Since the accuracy of the experiments at very large angles is rather low, the correction was neglected throughout.

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* Chadwick and Bieler, *loc. cit.*

† Darwin, 'Phil. Mag.,' vol. 27, p. 499 (1914).

In the case of light atoms like aluminium and magnesium, at angles between 60° and 100°, the ratio of the number of particles in the direct and scattered beams is of the order of 100,000 to 1. It was therefore impracticable to use the wheel-and-slit method of comparison used by Chadwick. Gold, whose nuclear charge is accurately known, and whose scattering over a large range of angles has been tested, was therefore used as a standard, and the scattering of the other metals compared with it. This method had the additional advantage that it was not necessary to make a correction for a possible change in the efficiency of the screen with the angle of incidence of the particles.

Since, under the inverse-square law, the scattering from thin foils of different materials under the same geometrical conditions varies as ntb^2 (Formula 1), the theoretical ratio of the scattering due to similar foils of the light meta under consideration and of gold is

$$r_t = \frac{n_m t_m b_m^2}{n_a t_a b_a^2} = \frac{n_m t_m \mathrm{N}_m^2}{n_a t_a \mathrm{N}_a^2} \cdot \frac{\mathrm{V}_a^4}{\mathrm{V}_m^4} \tag{1}$$

where the suffix m refers to the light metal, and the suffix a to gold.

If A_a, A_m are the atomic weights, and w_a, w_m the masses per unit area of the foils used, then,

$$r_t = \frac{w_m \mathrm{N}_m^2}{w_a \mathrm{N}_a^2} \cdot \frac{\mathrm{A}_a \mathrm{V}_a^4}{\mathrm{A}_m \mathrm{V}_m^4}. \tag{2}$$

The velocities V_a, V_m are the mean velocities of the α-particles in their passage through the foils. By an application of Geiger's law connecting the velocity of an α-particle with its remaining range, it is easily seen that this mean velocity is given by

$$\mathrm{V} = \sqrt[3]{\left(\frac{\mathrm{R}_o - (l_c + \frac{1}{2} l_f) \sec \bar{\phi}/2}{\alpha}\right)}$$

where $\bar{\phi}$ is the mean angle of scattering, $\mathrm{R}b$ the initial range of the particles, l_c, l_f are the air equivalents of the collodion film and the scattering foil respectively, and α is a constant.

Thus, r_t can be calculated from known quantities, and compared with r_e, the experimental ratio of the number of particles scattered by the light metal and by gold. Since the scattering from gold follows the inverse-square law, the ratio r_s/r_t is the ratio of the actual scattering due to the light metal to that which would be obtained if the inverse-square law were obeyed at all distances.

The larger foils were weighed on a chemical balance and the mass per area was deduced. The foils used with apparatus A were too light to be weighed with sufficient accuracy on a chemical balance. A convenient micro-balance devised by Mr. P. Kapitza, of the Cavendish Laboratory, had to be resorted to. The weight was determined in terms of the pull of a current on a piece of magnetized tungsten-steel wire. The current was read on a milliammeter, and the instrument was calibrated by means of known small weights. The instrument enabled one to weigh foils of the order of a few tenths of a milligram to 1 per cent.

The magnesium foils used were first carefully rubbed over with the finest emery paper and then with rouge paper; they were then weighed and placed on their frame. Between experiments, they were kept in a desiccator filled with nitrogen, purified by bubbling through two bottles containing a solution of pyrogallic acid and sodium hydroxide.

With gold, one or two thicknesses of the finest leaves obtainable were used. The correction for loss of velocity was small and easily determined to a sufficient accuracy. With aluminium four or five thicknesses of leaf were used, giving a stopping power of about 5 mm. of air. In this case, it seemed fair to assume that the unevennesses in the foils would more or less compensate each other, and that the thickness of the material could be taken as uniform in calculating the correction. With magnesium, however, the thinnest foil that could be rolled out had a stopping power of 12·5 mm. of air. A single thickness had to be used and the material was therefore much more uneven than the aluminium. It is therefore probable that the velocity correction as calculated is slightly too low.

The method of counting was the same as in Chadwick's* experiments. For the faster particles a source of Ra (B + C) deposited on a brass button was used; for the slower, a source of polonium on a nickel button was used. This source possessed the great advantage that there was no general lighting-up of the screens, due to β and γ rays, and that no correction for decay was required.

In most experiments two observers took turns at the counting. While the writer was measuring the source after removal from the emanation, the other observer would be in the darkened counting-room. By the time the apparatus was evacuated his eyes would be accustomed to darkness, and he could start counting, until the writer himself was ready. The two observers would then take turns at the microscope, counting for a minute at a time, with half-minute intervals. The time signals were given by a clock, which rang an electric bell every half-minute. In some of the experiments the writer did all the counting himself, using right and left eye alternately, the source being brought in to him when his eyes were fully accustomed to darkness. All alterations to the apparatus during the course of a count were made by means of pea lamps properly shaded to give just enough light where it was wanted.

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* Chadwick, *loc. cit.*

In order to minimise as far as possible the effect of an irregular decay of the source, and of a gradual variation in the efficiency of counting during an experiment, a series of counts on a light metal was bracketed by two series of counts on gold, and the thicknesses of the scattering foils so graduated as to give a similar number of particles per minute in each series, preferably between 30 and 40. The source was measured again at the end of the experiment.

§ 3.—*The Apparatus.*

Two types of apparatus were used, the same in principle, but differing in detail. Apparatus A was used for angles up to 25°, apparatus B for the larger angles.

Apparatus A.—The apparatus (fig. 2) consisted in an airtight brass box 12 cm. long. The section at right angles to the length was a square of 6 cm. side. One end was fitted with a flange FF′, ground down to fit a piece of plate-glass G. A slide C, which could be removed for purposes of adjustment,

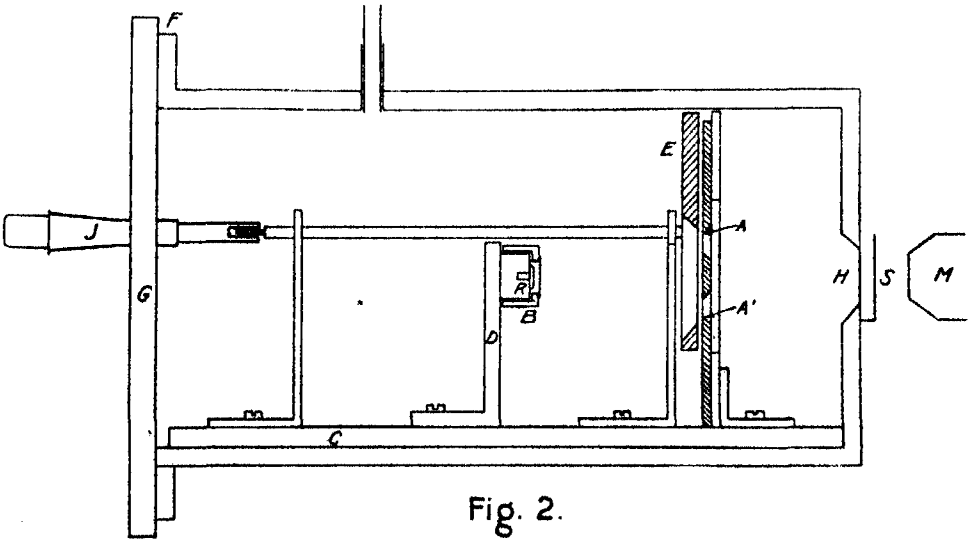


Fig. 2.

carried the source and scattering foils. A hole H, of 6-mm. diameter, at the end of the box and in its axis, was closed by a thin sheet of mica, of 1·8 cm. air-equivalent.

The source R was carried on a standard D screwed down to the slide. A small brass cap B, with a hole, covered by a film of collodion of less than 1 mm. stopping power, served to prevent any recoil atoms from the Ra A left on the source from escaping into the box, and to retard the diffusion of any small quantity of emanation which might not have been removed from the source. With this precaution it was possible to keep the radio-active contamination of the interior of the box to one or two scintillations per minute on the screen. This could be tested for by taking a few counts while the α-ray beam from the source was cut off by a magnetically-operated shutter just in front of the source.

The scattering foils were carried on a brass wheel E, with three holes, over two of which the foils were stretched. The third hole was left uncovered, to allow one to correct for the scattering by the edge of the diaphragm AA′. The wheel was turned from outside by a ground-glass joint J. A pawl, engaging in notches in the edge of the wheel, stopped it in the proper scattering position.

The diaphragm AA′, with a circular hole and a circular centre-piece, served to limit the scattered beam. In order to minimize the scattering from the edge, this diaphragm was made of pure graphite, kindly furnished by the Achèson Carbon Company. The centre-piece was waxed to two thin glass fibres stretched across the hole.

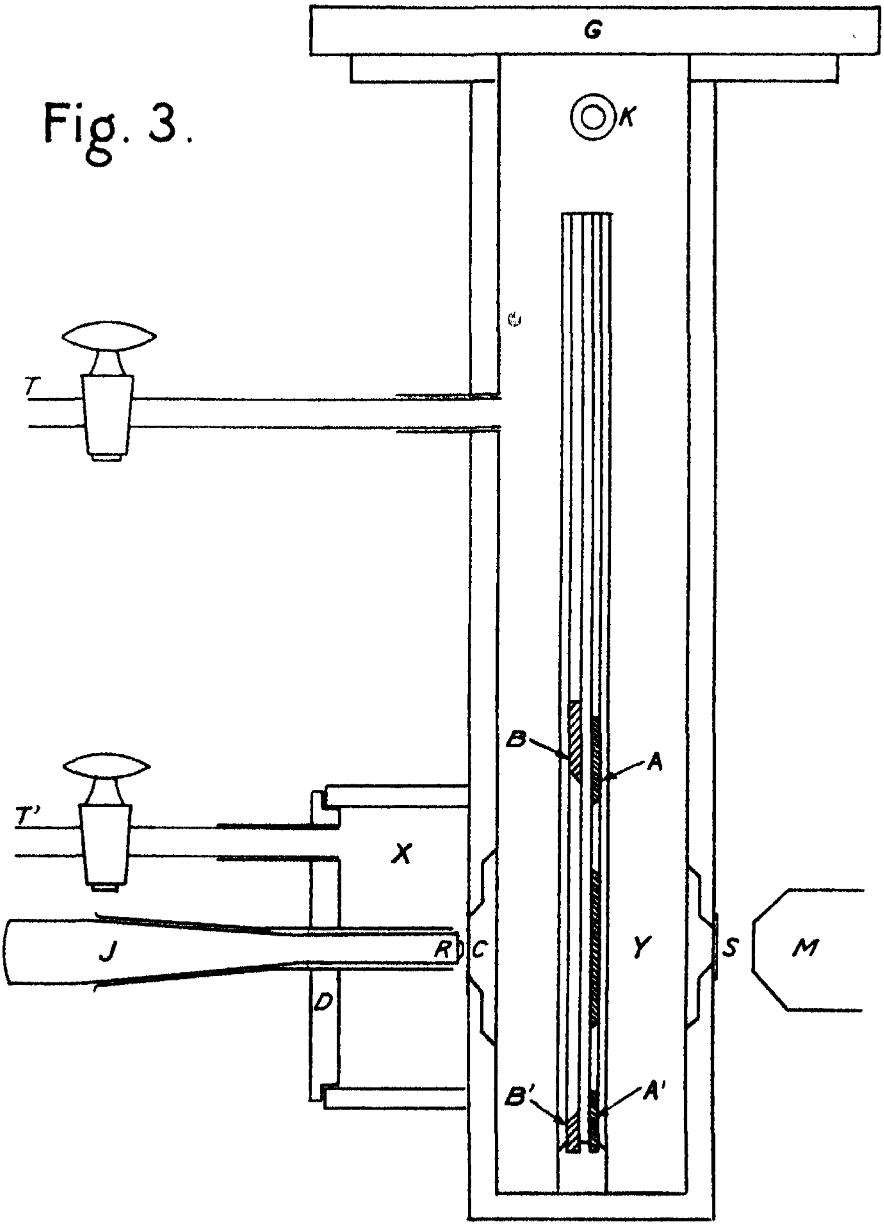
The zinc-sulphide screen S was placed outside the hole in the end of the box, and sufficient space was left between it and the box to insert mica absorbing sheets.

The microscope M had a Watson holoscopic objective of 16 mm. focal length and ·45 numerical aperture. In connection with a Watson × 5 eye-piece, it gave a field of 3·1 mm. diameter. Besides its large field, an objective of fairly long focus has the additional advantage of a good depth of focus, thus ensuring sharp definition for all scintillations, wherever they occur in the thickness of the screen.

Apparatus B.—At the large angles, the number of particles scattered is so small that the slightest amount of radio-active contamination of the inside of the box is sufficient to completely spoil a count. Apparatus B (fig. 3) was designed to prevent the possibility of contamination in any part of the apparatus from which an α-particle could reach the screen directly.

The apparatus had two chambers, the one X, into which the source was introduced, and the other, Y, in which the scattering took place. These were separated by a film of collodion, C, of stopping power less than 1 mm. of air, as measured by the scintillation method. This film was prepared by allowing a few drops of celluloid solution in a mixture of equal parts of ether and

Fig. 3.



absolute alcohol*, to evaporate on a clean mercury surface. It was then removed by means of a heated brass ring covered with soft wax, and carefully waxed on the hole in the scattering chamber of the apparatus. The back D of the source chamber was made removable, so as to allow a broken collodion film to be replaced. The two chambers were exhausted at the same time through tubes T and T′, connected to an oil pump by means of long rubber tubes. The size and length of the tubes had to be carefully adjusted, so that the pressure remained practically the same in the two chambers throughout the process of pumping. A U-tube manometer enabled one to see that the allowable difference of a few millimetres between the two sides was not exceeded while the apparatus was being exhausted. The collodion film was by far the most troublesome part of the apparatus, but it enabled one to obviate contamination completely. The experiments could not have been carried out without such a device.

The arrangement of source, scattering foil, diaphragm, and screen was exactly the same in principle as in Apparatus A, but the construction was quite different.

The source R fitted in a hole at the end of the male part of a ground-glass joint J. The scattering foil frame BB′ and the carbon diaphragm AA′ stood in vertical grooves and were provided with hooks, so that they could easily be taken out and replaced on removing the glass top G of the box. In addition, the foil frame was attached by means of a thread to the axle of a ground-glass joint at K, so that it could be lifted out of the way into the upper part of the box when the scattering due to the edge of the diaphragm was being determined.

The zinc-sulphide screen S was waxed on a hole in the side of the box. The microscope M was the same as the one used with the other apparatus.

§ 4. *Experimental Results.*

With the two types of apparatus, four carbon diaphragms were used in the experiments. They were so made that the maximum scattering angle, ϕ_2, of the one was as nearly as possible the same as the minimum scattering angle, ϕ_1, of the next larger. The dimensions and corresponding scattering angles are given below :—

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* The method was taken from a paper by F. Holweck, 'Ann. de Phys.,' vol. 17, p. 20 (1922). A solution of 100 mg. of celluloid in 10 c.c. of alcohol and 10 c.c. of ether gave films of about 0·8 mm. air equivalent.

Table I.

Diaphragm.	Inner Radius.	Outer Radius.	Apparatus.	Distance. RS.	ϕ_1.	ϕ_2.
	cm.	cm.		cm.	°	°
I	0·460	0·621	A	5·94	17·6	23·6
II	0·325	0·630	B	3·10	23·7	44·2
III	0·625	0·890	B	3·10	43·9	59·7
IV	0·900	1·830	B	3·10	60·3	99·5

The results obtained with aluminium and magnesium are given in Tables II and III below.

Table II—Aluminium.

Diaphragm.	RaC α-Particles.			—Mean Range 6·6 cm.			
	Angles.		Theoretical Ratio.	Experimental Ratio.	Particles counted.		Ratio.
	°	°			Al	A	
I	17·6	23·6	0·207	0·207	2,050	1,650	1·00 ± 0·03
II	23·7	44·2	0·210	0·197	3,800	4,775	0·94 ± 0·02
III	43·9	59·7	0·206	0·161	3,900	5,350	0·78 ± 0·02
IV	60·3	99·5	0·208	0·148	2,625	4,500	0·71 ± 0·02
	Polonium α-Particles.			—Mean Range 3·4 cm.			
III	43·9	59·7	0·216	0·217	2,545	2,690	1·00 ± 0·03
IV	60·3	99·5	0·219	0·203	1,435	2,075	0·93 ± 0·03

Table III.—Magnesium.

Diaphragm.	RaC α-Particles.			—Mean Range 6·2 cm.			
	Angles.		Theoretical Ratio.	Experimental Ratio.	Particles counted.		Ratio.
	°	°			Al	A	
I	17·6	23·6	0·210	0·214	1,875	2,150	1·02 ± 0·03
III	43·9	59·7	0·213	0·191	2,095	2,115	0·90 ± 0·03
IV	60·3	99·5	0·219	0·151	1,755	2,390	0·69 ± 0·02
	Polonium α-Particles.			—Mean Range 3·0 cm.			
III	43·9	59·7	0·243	0·256	650	440	1·05 ± 0·06
IV	60·3	99·5	0·259	0·204	360	160	0·79 ± 0·08

The probable errors given are those introduced by the probability distribution of the particles only. If Z particles are counted, the probable error due to the distribution is $1/\sqrt{Z}$. This is called the counting error.

In addition to this, there is the error in the weighing of the foils. In the case of very small foils, with which this would amount to at least 1 per cent., new foils were used in about every second experiment. This should bring the weighing error to less than 1 per cent.

A further cause of uncertainty is the possible unevenness of the foils. A square piece of a metal leaf was cut, measured, weighed and waxed on a brass frame. The area used in a scattering experiment was an annular ring, whose area was only a portion of that of the square foil. It is difficult to estimate the probable value of the error introduced by the fact that the mean thickness of the area used may not be the mean thickness of the whole foil. But, like the error in weighing, this error will be diminished by frequently changing the foils.

In the experiment at the larger scattering angles (60° to 100°) a source of 5 or 6 mg. equivalent of RaC had to be used. The direct α-rays were largely absorbed by means of a lead centre-piece in the carbon diaphragm, but there was still considerable lighting up of the screen due to scattered β-rays and secondary β-rays due to the γ-rays. The counting efficiency would on that account be somewhat lowered, but the effect would be the same with the gold particles as with those scattered by the light metal. The probable error is somewhat increased thereby, but there is no systematic error introduced.

It was feared at first that some of the apparent decrease in the number observed at large angles of scattering with the light metals might be due to the loss of energy in scattering making the particles less visible than those scattered by gold. But the fact that the decrease is distinctly less for the polonium particles than for the larger range RaC particles shows definitely that this is not the case. The loss of energy in scattering would have a larger effect on the visibility of the polonium particles than on that of the RaC particles.

The results are shown graphically in figs. 4 and 5. The vertical lines indicate the angular limits of the diaphragms used. The full horizontal lines give the ratio for each diaphragm ; the dotted lines are at a distance from them equal to the probable error in counting. The curves have been drawn so as to make the area under the curve between the vertical lines as nearly as possible equal to that under the full horizontal lines. When this is not possible, it has been the object to make the difference between these areas not much greater than the counting error. The results for magnesium with polonium α-particles have not been plotted, because the total absorption in the scattering foil was such a large proportion of the initial range as to make them untrustworthy.

In all cases the curves indicate that the scattering at small angles is, very approximately, that which would be expected on the inverse-square law, indicating that this law is obeyed at large distances from the nucleus.

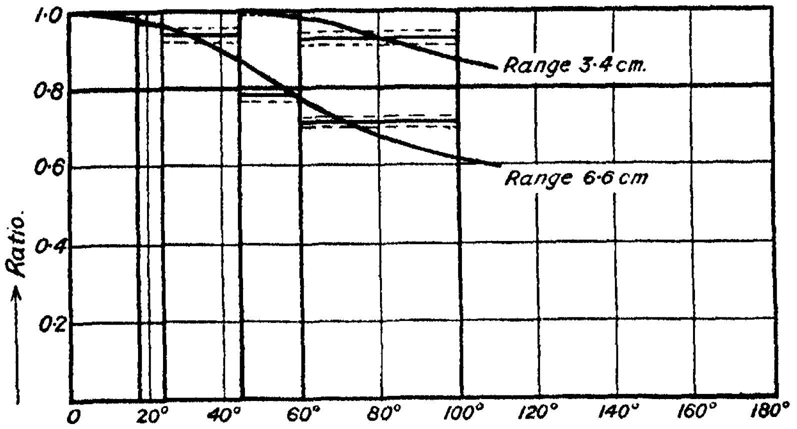

Fig. 4.

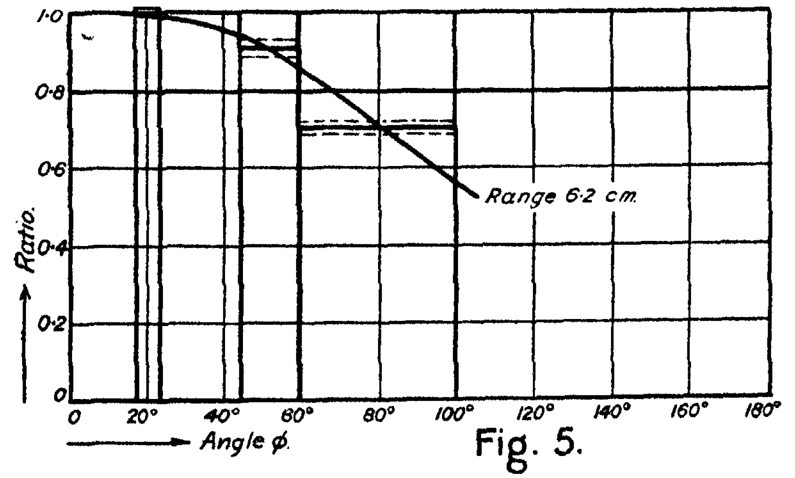

Fig. 5.

As the angle increases, the ratio of the actual scattering to what would be expected on the inverse-square law diminishes rapidly. This suggests the existence of an attractive force at short distances from the nucleus, which partly neutralises the electrostatic repulsion of the α-particle by the nucleus. The suggestion is further borne out by the fact that the slower α-particles from polonium, which do not penetrate so close to the nucleus, follow the theoretical law of scattering more closely. The question will be discussed more fully in the next section.

§ 5. *Discussion of Results.*

The author has published elsewhere* a discussion of the effect of an attractive force, varying as a higher power of the distance than the second, on the scattering of α-particles, and has given curves showing the distribution of scattered particles when this additional attractive force varies as the cube or the fourth-power of the distance. In both these cases the number scattered is lower at the higher angles than under the pure inverse-square law, and the decrease is approximately proportional to a parameter called x in the inverse-cube case, and y in the inverse fourth-power case, which depends on the energy of the α-particles and on the ratio of the attractive force potential to the ordinary electrostatic potential. In fact, x varies directly as the energy of the α-particles, and y as the square of the energy.

In the case of aluminium, experimental curves have been obtained for particles of two different ranges, 6·6 cm. and 3·4 cm., and therefore two different energies, and we are able to decide at once whether an additional attractive force of the kind considered theoretically will account for the facts.

A glance at fig. 4 of this paper, and at fig. 4 of the theoretical paper, shows at once that the actual distribution is not unlike what would follow from an additional inverse fourth-power law attractive force. In particular, the two figures show the same small divergence from the inverse-square law distribution at the smaller angles. Both curves have a horizontal tangent at the origin; the inverse-cube law has not.

A consideration of the ratio of the energies $K_{6\cdot 6}$ and $K_{3\cdot 4}$ of the two classes of particles used also decided in favour of a law approximating to the inverse fourth-power for the additional force. By an application of Geiger's law connecting the range of an α-particle with its velocity, we can easily determine this ratio and obtain

$$\frac{K_{6\cdot 6}}{K_{3\cdot 4}} = \left(\frac{6\cdot 6}{3\cdot 4}\right)^{2/3} = 1\cdot 56 \quad \text{and} \quad \left(\frac{K_{6\cdot 6}}{K_{3\cdot 4}}\right)^2 = 1\cdot 56^2 = 2\cdot 42.$$

These two figures give approximately the ratio of the distributions on the inverse-cube, and inverse fourth-power law to the ordinary inverse-square law distribution. Now, the ratio of the departures in the experimental curves is approximately 3. We may conclude that divergence from the inverse-square law at short distances from the nucleus approximately follows the inverse fourth-power law.

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* Bieler, 'Proc. Camb. Phil. Soc.,' vol. 21, p. 686 (1923).

The experimental curve for particles of 6·6 cm. range may be fitted approximately by an inverse fourth-power law curve for which $y = 0{\cdot}6$. Since the additional force is attractive, and varies more rapidly than the electrostatic repulsion, there will be a distance at which the total force on the α-particle would vanish. It is shown in the theoretical paper referred to that this distance is given by

$$r = \frac{2NE_e}{MV^2}\sqrt{\frac{3}{4}y}.$$

If $y = 0{\cdot}6$ for an α-particle of 6·6 cm. range, this formula gives

$$r = 3{\cdot}44 \times 10^{-13} \text{ cm.}$$

Within this distance from the centre of the nucleus, the attractive force will be larger than the electrostatic repulsion of the parts of the nucleus. This distance may therefore be considered as the effective radius of the nucleus. The estimate seems small at first for a nucleus which contains fourteen electrons and twenty-seven protons. Some of the electrons may, however, be outside this radius, for electrostatic attraction alone will be sufficient to maintain them in the nucleus. The fact that, on this law, the calculated apsidal distance of an α-particle of 7 cm. range, deflected through 180°, is $4{\cdot}6 \times 10^{-13}$ cm., seems to show, however, that the estimate is not much too low. Such an additional inverse fourth-power attractive force would diminish very rapidly with the distance from the nucleus. At $3{\cdot}44 \times 10^{-12}$ cm. it would be only 1/100 of the electrostatic force, and at 10^{-10} cm. less than 1/80000. It would not therefore have a noticeable effect on spectral lines.

It was thought at first that the experiments might show some difference between the behaviour of aluminium and of magnesium. Sir Ernest Rutherford and Dr. Chadwick* found that swift H-nuclei, of forward range about 90 cms. of air, were liberated from the aluminium nucleus, whereas they did not find a trace of particles of range greater than 30 cms. in magnesium. They explained the result by assuming that in atoms which can be artificially disintegrated there are H-nuclei present outside the main part of the nucleus, as close satellites describing orbits round it. If such satellites are present in aluminium and not in magnesium, it might be expected that they would manifest themselves in some difference between the scattering by these two elements when the collision is very close. The curves for aluminium and magnesium are, however, similar within the experimental error, and no conclusion can be drawn in this respect from the experiments.

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* Rutherford and Chadwick, *loc. cit.*

It would be interesting to repeat these experiments with the fastest α-particles obtainable, namely, those from ThC, of range 8·6 cm. They are, however, always produced together with particles of 4·8 cm. range. Owing to the fact that very wide beams have to be used in order to obtain a measurable effect n cases where the scattering is so small, it has seemed to the writer that it was not possible to separate the two classes of particles satisfactorily.

The writer has made an attempt to explain on a magnetic hypothesis this inverse fourth-power term in the law of force. If the particles composing the nucleus and the α-particle describe orbits, it is natural to assume that they have a magnetic moment. Two magnetic doublets will attract if they are in the proper relative orientation, and the law of force will be the inverse fourth-power. A rather artificial mechanism had to be postulated, however, to allow the α-particle to assume the proper orientation for attraction to take place, and the orbital velocities necessary to give a sufficient magnetic moment were so large as to make the relativity increase in mass incompatible with the whole-number law of atomic weights.

In conclusion, the writer wishes to thank Sir Ernest Rutherford, in whose laboratory this work was carried out, for his constant inspiration and encouragement, and several of the research students at the Cavendish Laboratory for help in the very tedious work of counting. His thanks are also due to Mr. G. R. Crowe for the preparation of the radio-active sources used.

The Crystalline Structure of Succinic Acid, Succinic Anhydride and Succinimide.

By Kathleen Yardley, M.Sc.

(Communicated by Sir William Bragg, F.R.S. Received January 10, 1924.)

Succinic acid, COOH . CH_2 . CH_2 . COOH, is a dibasic acid which crystallises in a form belonging to the monoclinic holohedral class.

Groth (' Chemische Krystallographie,' Part III, p. 262) gives the following crystallographic data concerning this crystal :—

$$a : b : c = 0{\cdot}5688 : 1 : 0{\cdot}6195$$
$$\beta = 91^\circ\ 20'.$$

On the other hand, the ' Elemente der Chemischen und Physikalischen Krystallographie, 1921,' gives :—

$$a : b : c = 0{\cdot}5747 : 1 : 0{\cdot}8581$$
$$\beta = 133^\circ\ 37'.$$

A brief consideration of these two sets of axial ratios shows that the same *a*, *b* axes have been taken for both, but that the (001) plane in the second set is the (101) plane in the first. There seemed to be no obvious advantage in using the elementary cell defined by the second set of axial ratios, hence the values given by Groth were used in the calculation of the spacings.

Some very fine crystals were obtained by slow recrystallisation from water at room temperature. Most of the crystals showed a combination of the basal plane {001} with the form {111}, all four faces of the latter form being well and equally developed. A few crystals also showed the planes {010} and sometimes {110} (small). Groth also records the occurrence of faces {011} and {121}, but these were not observed on any of the crystals grown.

A perfect cleavage was observed parallel to {010} and an imperfect cleavage parallel to {111}.

The crystal twins on {001}. Only a few real cases of twinning were observed, though parallel growths were very frequent. The crystals were soft and easily crushed, the melting-point, however, being as high as 185° C.

Observations of spacings in all the principal zones were made, using an X-ray spectrometer, together with a Coolidge tube of molybdenum anticathode.

Taking the mass of the H atom as $1 \cdot 64 \,.\, 10^{-24}$ grs., we may equate the two following expressions for the mass contained in the unit monoclinic cell :—

$$(a \,.\, b \,.\, c \sin \beta)\, \rho = n \,.\, \mathrm{M} \,.\, 1 \cdot 64,$$

where—

ρ = density of crystal,

n = number of molecules per cell,

M = molecular weight,

a, b, c being expressed in Ångström units.

A preliminary measurement showed that the spacing of the cleavage plane (010) was 8·92. We have also—

$$\rho = 1 \cdot 558 \text{ grs./c.c.}, \quad \mathrm{M} = 118 \cdot 1.$$

Hence, substituting in the above equation—

$$(8 \cdot 92)^3 \times 0 \cdot 5688 \times 0 \cdot 6195 \times \sin 91°20' \times 1 \cdot 558 = n \times 118 \cdot 1 \times 1 \cdot 64$$
$$\text{giving } n = 2 \cdot 01.$$

That is, there are two molecules in the unit cell. Considerations of symmetry show that the unit cell of a monoclinic holohedral crystal can only contain one, two, or four molecules (or an integral multiple of four), if based on the Bravais lattice Γ_m. In the case we have above, where $n = 2$, the cell contains only two differently oriented but similar molecules, A and B. ("similar" here means that A and B are either completely identical or that one is the mirror-image of the other.) There are three possible cases :—

(*a*) B may be brought into coincidence with A by a reflection in the symmetry plane, together with a possible translation parallel to the plane. In this case the molecule itself possesses a digonal axis parallel to the b axis.

(*b*) B may be brought into coincidence with A by a rotation through 180° about the digonal axis, plus a possible translation parallel to the axis. In this case the molecule itself possesses a plane of symmetry parallel to (010).

(*c*) B may be brought into coincidence with A by a reflection (plus a possible translation parallel to (010)) *or* a rotation (plus a possible translation parallel to b), in which case the molecule is centro-symmetrical.

The spacings to be expected for other planes in the crystal were calculated on the basis $n = 2$, and compared with the actual spacings found by the spectrometer method. No special care was taken in measuring relative intensities of reflection, for the sensitiveness of the methyl bromide used in the ionisation chamber varied so much as to render such measurements, in general, almost worthless for any accurate calculation. It was possible, however, to obtain the relative intensities of different order reflections for the same plane with a fair degree of accuracy.

Plane.	Spacing.		Comparative intensity of reflection.
	Calc.	Obs.	
100	5·06	2·54	Moderately large.
010	8·90	4·46	Very large indeed.
001	5·52	5·52	Moderate (IInd > Ist).
013	1·80	1·80	Moderate.
012	2·64	2·64	Small.
011	4·69	4·71	Mod. large (IInd > IIIrd > Ist).
021	3·46	3·46	Large.
201	2·28	2·28	Mod. small.
101	3·68	3·69	Mod. large.
102	2·40	?	Doubtful.
103	1·71	1·72	Small.
$10\bar{2}$	2·45	2·47	Mod. small.
$10\bar{1}$	3·77	3·79	Moderate.
$20\bar{1}$	2·32	2·33	Mod. large.
310	1·66	1·67	Small.
210	2·44	2·45	Small.
320	1·59	1·60	Very small.
110	4·41	?	Doubtful.
230	1·93	1·94	Mod. small.
120	3·34	3·30	Large.
130	2·56	1·28	Very small.
140	2·04	2·01	Very small.
111	3·41	3·43	Very large.
112	2·32	2·32	Small.
$11\bar{1}$	3·47	3·49	Very large.
212	1·81	1·82	Mod. large.
121	2·84	2·85	Very large.

These results are sufficient to make certain points very clear with regard to the structure. The main cleavage plane (010) gave no Ist order reflection, but an extremely large IInd order reflection; also the other odd orders were all absent, the relative intensities of the even orders being

$$\text{II} : \text{IV} : \text{VI} : \text{VIII} = 400 : 92 : 25 : 1.$$

That is, the intensity of reflection varies (very nearly) inversely as the square of the order involved. This seems to indicate that the (010) planes consist of flat layers of densely packed atoms, very few atoms lying between the (010) planes. No structure which does not fulfil this condition can be considered at all satisfactory.

Now, in the first place, we have to decide between two possible Bravais lattices, Γ_m and Γ'_m, as a basis of the crystal structure. The lattice Γ_m is the simple monoclinic lattice obtained by placing points at the vertices of a series of right prisms with parallelogrammatic bases, which are similar and similarly situated in space, each vertex being common to eight parallelepipeda. The lattice Γ'_m may best be regarded either as a monoclinic lattice with points at the centres of two opposite rectangular faces of the prisms, or as a centred monoclinic lattice, or as a face-centred monoclinic lattice. There are other ways of describing Γ'_m, but these are the only aspects which introduce a lattice having one edge perpendicular to the other two.

It may readily be seen that Γ'_m always has certain general planes, the spacings of which are halved. For instance, regarding the lattice as centred, we find that the spacings of the $\{hkl\}$ planes are halved in every case where $h + k + l$ is odd. Taking a vertex of the prism as origin and the crystallographic axes as axes of co-ordinates, the equation to the plane $\{hkl\}$ is

$$\frac{h}{a}x + \frac{k}{b}y + \frac{l}{c}z = 1.$$

The point at the centre of the lattice has the co-ordinates $\left(\frac{a}{2}, \frac{b}{2}, \frac{c}{2}\right)$, and lies *in* the plane $\{hkl\}$ if, and only if,

$$\frac{h}{a}\cdot\frac{a}{2} + \frac{k}{b}\cdot\frac{b}{2} + \frac{l}{c}\cdot\frac{c}{2} = 1,$$

that is, if $h + k + l$ is even.

If $h + k + l$ is odd, it lies in the half-way plane $\frac{h}{a}x + \frac{k}{b}y + \frac{l}{c}z = \frac{1}{2}$.

Similarly if Γ'_m be regarded as a monoclinic lattice having points at the centres of the (001) faces (where b is perpendicular to a and c), then the $\{hkl\}$ spacing is halved if $h + k$ is odd.

If Γ'_m be considered as a face-centred monoclinic lattice, the $\{hkl\}$ spacing is halved if $h + k$ or $k + l$ or $l + h$ is odd.

Now the observed spacings include sufficient general planes, whose spacings are all normal, to show that the adoption of Γ'_m as the fundamental space lattice in this case is not possible.

Since we must use Γ_m as a basis for our structure, and since there are only two molecules in each unit cell, it follows that the molecule itself must have two-fold symmetry as indicated above, either :—

(1) A digonal axis.
(2) A plane of symmetry.
(3) A centre of symmetry.

There are only four space-groups in the monoclinic holohedral class based on the lattice Γ_m, and the molecules in the unit cell of this crystal must be arranged so as to give all the elements of symmetry of one of these four space-groups. The particular space-group concerned, C_{2h}^1, C_{2h}^2, C_{2h}^4 or C_{2h}^5, can be determined only by means of the planes whose observed spacings are halved.

Not every kind of two-fold symmetry of the molecule is possible in each of these space-groups.

In C_{2h}^1 the molecules are arranged as in fig. 1, the elements of symmetry being a rotation axis perpendicular to a plane of symmetry. No spacings will be halved, and the molecule can only possess two-fold symmetry in the form of a plane or an axis. This space-group is ruled out because the (010) plane is very definitely halved.

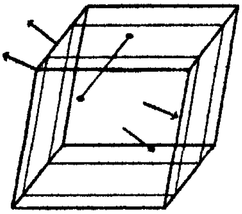


FIG. 1.

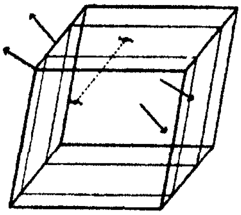
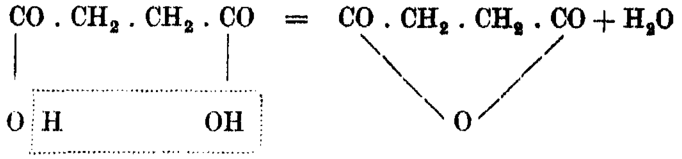


FIG. 2.

In C_{2h}^2 (fig. 2) the elements of symmetry are a screw axis perpendicular to a plane of symmetry. The (010) spacing only is halved, and the molecule may possess a plane or a centre (not a digonal axis). This is a possible arrangement.

The remaining groups C_{2h}^4, C_{2h}^5, which possess a rotation axis perpendicular to a glide-plane, and a screw axis perpendicular to a glide-plane, respectively, are not possible, because both involve the halving of certain series of planes in the $\{h0l\}$ zone, whereas all planes in that zone (with the exception of (100)) gave normal first-order reflections.

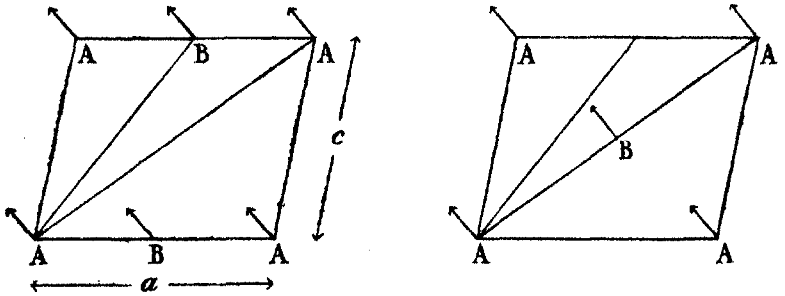
The crystal, therefore, is an example of the space-group C_{2h}^2. If the molecule has a centre of symmetry the position of the second (B) molecule in the cell is limited to the points $\left(0 \text{ or } \frac{a}{2}, 0 \text{ or } \frac{b}{2}, 0 \text{ or } \frac{c}{2}\right)$, taking the A molecule at the origin. One of these positions, namely $\left(0, \frac{b}{2}, 0\right)$, would cause the halving of (010) only, as required, but it is found to be almost impossible to fit the molecules into this position if the hitherto accepted values of the atomic sizes hold to within reasonably narrow limits. Moreover, succinic acid is one of the few dibasic acids that form an anhydride fairly easily. It is readily seen that if the anhydride is formed as follows :—



$$CO . CH_2 . CH_2 . CO(OH)(OH) = CO . CH_2 . CH_2 . CO(O) + H_2O$$

then the OH groups of one molecule will probably lie adjacent to one another in the crystal, and this would be impossible if the molecule were centro-symmetrical.

We are left with the probability of a plane of symmetry in the molecule itself. The B molecule will be so oriented that it can only be brought into coincidence with A by a rotation through 180° about the digonal axis, together with a translation of $b/2$ parallel to that axis. The (010) spacing is then halved, but no other spacing in the crystal. It may be pointed out at this stage that a " real " halving of the (100) or (001) spacings in a monoclinic holohedral cell (that is, a halving due to a reflection molecule in a suitable position) must necessarily halve some other spacings also. A rotation molecule can never halve any spacing but the (010). For example, if B be a reflection molecule and the diagrams below (fig. 3) represent the projection of the molecules in the cell on the plane (010),



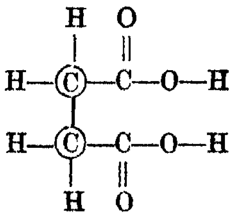
(*a*) (*b*)

FIG. 3.

then the halving of the (100) spacing also involves the halving of all planes {*hol*} where *h* is odd in the case (*a*), and of {*hol*} where $h + l$ is odd in the case (*b*).

Hence, although no odd order reflections were found for the (100) plane, only the IInd order, yet this cannot indicate a " real " halving, since full spacings (*i.e.*, Ist order reflections) were found for the planes (101), $(10\bar{1})$, (201), $(20\bar{1})$, $(10\bar{2})$, etc. The disappearance of the Ist order of the (100) reflection must be due to some accidental arrangement of the atoms with reference to this particular plane.

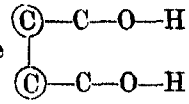
The structural formula of succinic acid may be written as follows :—

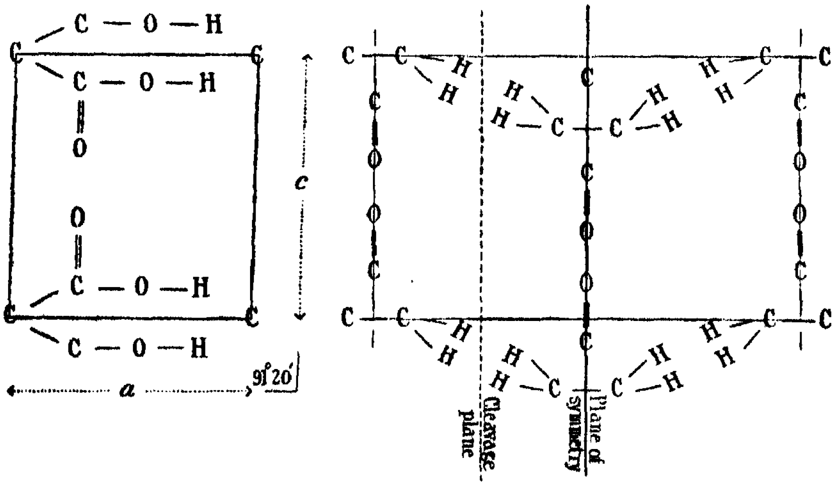


It seems reasonable to suppose that the atoms Ⓒ lie along the dyad axis, the molecular plane of symmetry passing between them. Moreover, some kind of tetrahedral arrangement of the four carbon atoms is to be expected.

W. L. Bragg has given the "atomic diameters" of oxygen and carbon as 1·30 and 1·54 Å.U. respectively. This would make the length $(O = C \; C = O)$ equal to $2 \, (1{\cdot}54 + 1{\cdot}30) = 5{\cdot}68$ Å.U.

W. T. Astbury, however, has shown that in tartaric acid and also in racemic acid the diameter of the ketonic oxygen is, in all probability, less than 1·30,[*] and if this holds also in the case of succinic acid, then this distance becomes very nearly equal to the length of the *c* axis, 5·52 Å.U.

It is found, in fact, that the molecule, considered as a space-grouping of atoms, fits very well into the unit cell if we suppose that the  groups



(a) (b)

FIG. 4.

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[*] 'Roy. Soc. Proc.,' A, vol. 102, p. 522; also vol. 104, p. 219.

lie along the *a* axis and the O = C / C = O group along the *c* axis, the junction with the B molecule being made by hydrogens only. It appears that junctions between hydrogens are usually weak, which would account for the very perfect cleavage parallel to the {010} plane.

The plane of symmetry of the molecule itself is shown most clearly in fig. 4 (B).

It is not possible to fix accurately the position of the second (B) molecule in the cell beyond the fact that it lies in the plane (020). At the present stage a consideration of relative intensities of reflections from different planes can give us very little help, since when the molecule contains many atoms we cannot interpret the intensities at all. The fact that the (021), (120) and (121) planes all give very intense reflections seems to indicate that if the molecule be considered as a single scattering centre, the second molecule would lie somewhere near to the point B (fig. 5), but as a matter of fact the molecule is an extended structure. More probably the centre of gravity of the second molecule lies in the (111) plane, and also, of course, in the (020), since the (111) is an outstandingly good reflector, besides being a crystal face and an imperfect cleavage plane. In such a structure the distance between the linking H nuclei is about 1·1 Å.U, which agrees quite well with hitherto accepted values for the H diameter.

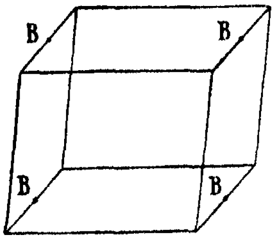


Fig. 5.

The structure suggested also gives the following atomic dimensions :—

C diameter	= 1·54 Å.U.
Ketonic O diameter	= 1·22 Å.U.
Length of (OH) group	= 2·5 Å.U.

The frequent twinning recorded by Groth (twin plane {001}) receives a

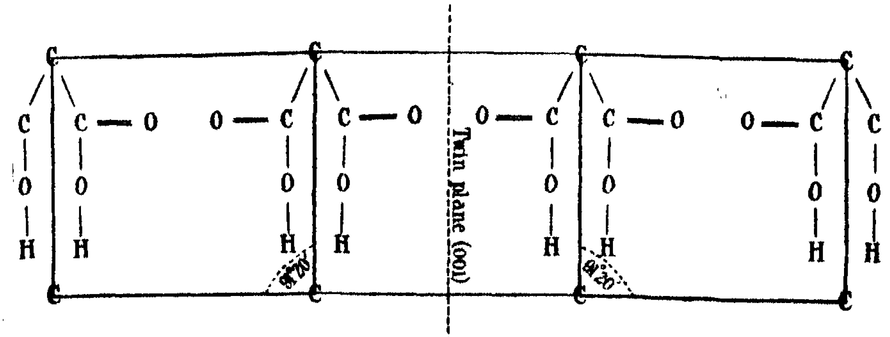


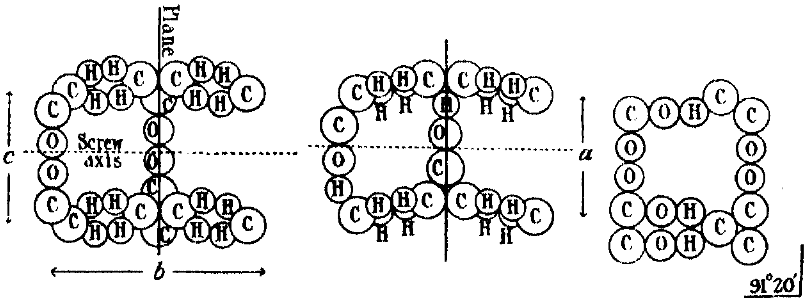
Fig. 6.

ready explanation on the basis of the above structure, as will be seen from a study of fig. 6, which gives the diagrammatic representation of such a twin.

There is a striking resemblance between this structure and that previously suggested by W. T. Astbury* for the twin of racemic acid. Although the latter is a triclinic crystal, in each case the frequent twinning is accounted for by a mirror-image junction between the ketonic oxygens.

There is no need to suppose any obliquity in the tetrahedral arrangement of the C atoms, either in the succinic acid molecule or in that of succinimide considered later.

The actual appearance of the crystal as projected on the three axial planes is shown in fig. 7 (A), (B), (C).



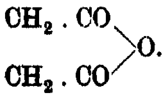
(A) {100} plane. (B) {001} plane. (C) {010} plane.

FIG. 7.

The actual position and arrangement of the H atoms cannot, of course, be settled, as these are single nuclei, and therefore are too light to effect any appreciable scattering of X-rays.

In order to account for the monoclinic angle $\beta = 91° 20'$, we must suppose that the ketonic oxygens are attached slightly obliquely to their appropriate carbons. This fact will be more emphasised when we discuss the structure of succinimide.

The following data are given by Groth concerning succinic anhydride,



$$\begin{matrix} CH_2 . CO \\ CH_2 . CO \end{matrix} \Big> O.$$

Orthorhombic (class ?). Melting-point, 119° C.

$a : b : c = 0{\cdot}5947 : 1 : 0{\cdot}46225.$

The molecular weight is 100. The specific gravity was not given and was therefore determined, roughly, first by the usual specific gravity bottle method, and then more accurately by suspending small crystals (free from air) in a mixture of benzene and methylene iodide. The density of the solution could be varied by varying the proportion of the constituents until the crystals remained almost at rest, suspended in the solution, whose density was immediately found. The latter method gives for the specific gravity ρ :—

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* 'Roy Soc. Proc.,' vol. 104, p. 233.

$$1 \cdot 508 > \rho > 1 \cdot 501.$$

A Coolidge tube with a rhodium anticathode was used, together with the X-ray spectrometer, to determine the spacings. A difficulty was encountered to begin with, in that the crystal class had not been previously determined. The crystals were difficult to grow, and the few good crystals that were obtained (from acetone) were small. They definitely belonged either to the hemimorphic or the holohedral class of the orthorhombic system. It was hoped that the X-ray measurements might assist in deciding between these two classes. For example, if it had been found that the unit cell contained eight molecules, and also that none of the general planes were halved, it would be reasonably certain that the crystal belonged to the holohedral class, and was based on the lattice Γ_o. It was found, however, that the cell contained only four molecules, all the general planes examined showing normal spacings. This might mean either :—

(*a*) That the crystal belonged to the holohedral class, the molecule itself having two-fold symmetry.

(*b*) That the crystal belonged to the hemimorphic class, the molecule being asymmetric.

Only in very special cases (*i.e.*, if there are halvings in all three of the axia zones, but none among the general planes) is it possible by means of X-ray measurements to decide between these two alternatives.

The crystal used showed a well-developed *c* zone, but grew none of the axial planes as faces; there was no cleavage plane. The reflection from the (001) plane was first found, and the spacing proved to be 5·41 Å.U. Using the known axial ratios and taking the specific gravity as 1·505, we find, as before :—

$$\text{Mass contained in unit rhombic cell} = a \,.\, b \,.\, c \,.\, \rho = n\,\mathrm{M} \,.\, 1 \cdot 64,$$

a, *b*, *c* being expressed in Ångström units.

Hence $n = 4 \cdot 04$ (*i.e.*, 4 molecules per cell).

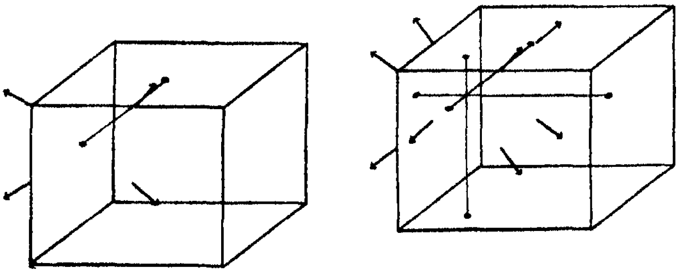
It may here be noted that the X-ray spectrometer method can be used also to measure the angles between planes, even though the planes are not faces on the crystal used. The crystal of succinic anhydride was so small, and the faces so dull, that it was not easy to weigh up the crystal with certainty before using it—

in fact, the probable direction of the *c* axis was the only thing known. Starting from this, however, the apparatus was employed as a goniometer, X-rays being used instead of visible light, and the angles between 20 distinct pairs of planes were determined and compared with the values calculated from the axial ratios and the indices of the planes. The difference was generally less than 10 minutes of arc, although no particular care was taken over the accuracy of this part of the work. This served not only to identify the planes whose spacings were being found, but also to identify the actual faces on the crystal, and to verify the axial ratios given by Groth. In fact, no previous crystallographic data are really necessary at all if good small crystals can be grown. The X-ray method fails, however, in general, to determine the *class* to which a crystal belongs.

The observed spacings compared with the calculated values are as follows :—

Plane.	Spacing.		Comparative intensity of reflection.
	Calc.	Obs.	
100	6·93	6·95	Moderate (IInd > Ist).
010	11·66	2·91	Small.
001	5·39	5·41	Mod. small (IInd > Ist).
013	1·78	1·75	Small.
012	2·63	2·63	Moderate.
023	1·72	1·65	Very small (doubtful reflection).
011	4·89	4·89	Moderate.
032	2·22	2·22	Small.
021	3·96	3·95	Mod. large.
031	3·15	3·15	Mod. small.
041	2·56	2·57	Mod. small.
301	2·12	2·10	Very small (doubtful reflection).
201	2·92	2·91	Mod. large.
302	1·75	1·76	Small.
101	4·26	4·26	Very large.
102	2·51	2·51	Moderate.
103	1·74	1·75	Small.
410	1·71	1·71	Small.
310	2·27	2·27	Mod. small.
210	3·32	3·32	Moderate.
320	2·15	2·16	Small.
430	1·58	1·57	Small.
110	5·96	5·97	Large (IInd > Ist).
120	4·46	4·45	Large.
140	2·69	2·63	Very small (doubtful reflection).
111	4·00	4·01	Very large.
112	2·46	2·46	Moderate.
113	1·72	1·72	Small.
221	2·61	2·61	Mod. large.
331	1·86	1·87	Moderate.
121	3·44	3·35	Small } Crystal slightly out of adjustment.
122	2·31	2·27	Moderate

Here we see that only one plane does not give a first order reflection, and that is the (010), which appears to be quartered, since only a fourth order reflection was found. Now, in the orthorhombic hemimorphic and holohedral classes, it is not possible for one spacing only to be quartered or even halved, except by an accidental arrangement of the scattering centres relatively to that plane. The crystal, therefore, since no other spacings are halved, must belong either to the space-group C_{2v}', or to the space-group Q_h'. The diagrammatic arrangement of asymmetric molecules in these groups is shown in fig. 8 (A) and (B).



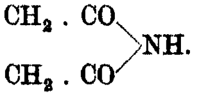
(A) C_{2v}'. (B) Q_h'.

Fig. 8.

In the group c_{2v}' there are two planes of symmetry perpendicular to each other meeting in a digonal axis. In the group Q_h' there are three mutually perpendicular planes of symmetry meeting in three digonal axes. Moreover, in this group the only two-fold symmetry that the molecule can possess is a plane (not an axis or a centre) parallel to any one of the axial planes.

The possession of a plane of symmetry by the succinic anhydride molecule would seem to fit in well with the fact that the succinic acid molecule also has a plane of symmetry, but in view of the uncertainty as to the crystal class, no attempt will be made in this paper to fix the absolute structure of succinic anhydride.

Groth gives the following data for succinimide,



$$\begin{matrix} CH_2 . CO \\ CH_2 . CO \end{matrix} > NH.$$

Rhombic bipyramidal (*i.e.*, orthorhombic holohedral). Melting-point 129°.

$$a : b : c = 0 \cdot 7888 : 1 : 1 \cdot 3655.$$

The molecular weight is 99.

Crystals were grown with difficulty from acetone, only one or two being obtained that were suitable for examination. These were bipyramids with faces {111}, and the subordinate faces {001}, {110}, {102}, {201}. A tendency to cleave was observed, but owing to the smallness and irregularity of the crystals, the cleavage plane could not be definitely determined.

It was found that the three axial planes had the following spacings :—

$$\left.\begin{aligned} a &= 7{\cdot}50\ \text{Å.U.} \\ b &= 9{\cdot}60\ \text{Å.U.} \\ c &= 12{\cdot}75\ \text{Å.U.} \end{aligned}\right\}\ \text{I.}$$

The density was determined by the suspension method to be 1·419 grs./cc.

Mass contained in unit cell $= 7{\cdot}50 \times 9{\cdot}60 \times 12{\cdot}76 \times 1{\cdot}419.$

$$= n \times 99 \times 1{\cdot}64.$$

Hence $n = 8{\cdot}03$ (*i.e.*, 8 molecules per cell).

These values for a, b, c, however, give for the axial ratios :—

$$a : b : c = 0{\cdot}781 : 1 : 1{\cdot}329,$$

which differs considerably from the data given by Groth :—

$$a : b : c = 0{\cdot}7888 : 1 : 1{\cdot}3655 \text{ (Bunge, 1869).}$$

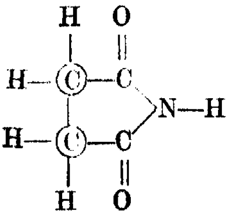
This discrepancy is outside the limit of experimental error in the X-ray method, therefore the other spacings were calculated from the observed value of the axial ratios and compared with observation. Taking $n = 8$ exactly, we have :—

Plane.	Spacing.			Comparative intensity of reflection.
	Calc. from Groth's ratio.	Calc. from obs. ratio.	Obs.	
100	7·47	7·49	3·75	Very large.
010	9·47	9·59	4·80	Large.
001	12·94	12·75	12·75	Mod. large (IVth > IInd > Ist).
011	7·64	7·66	7·60	Mod. small.
012	5·34	5·30	5·32	Mod. large.
021	4·45	4·49	4·49	Mod. large.
023	3·19	3·18	3·22	Mod. large.
104	2·97	2·94	2·94	Small IInd (Ist ?).
102	4·89	4·86	4·88	Moderate.
101	6·48	6·47	6·50	Moderately large.
302	2·32	2·37	2·34	Mod. small.
201	3·59	3·60	3·58	Moderate.
130	2·91	2·94	2·95	Moderate.
120	4·00	4·04	4·05	Small (IInd > Ist).
230	2·41	2·43	2·44	Moderate.
110	5·87	5·91	5·97	Mod. large.
210	3·47	3·55	3·55	Mod. large.
111	5·34	5·37	5·37	Mod. large.
112	4·35	4·34	4·32	Large.
221	2·86	2·88	2·88	Mod. small.
211	3·36	3·37	3·38	Mod. large.
212	3·06	3·06	3·09	Large.
123	2·93	2·93	2·95	Moderate.
121	3·82	3·86	3·70 (?)	Moderate.

Here none of the general planes are halved (or doubled), hence the fundamental Bravais lattice is Γ_0. The (100), (010) are the only planes which appear to be halved. Now there is no space-group in the orthorhombic holohedral class, in which two spacings only are halved; either no spacings at all are halved (Q_h'), or else sets of planes show half-spacings (such as $\{okl\}$ if $k + l$ is odd, in Q_h^2, etc.).

Since Ist order reflections were found for all the principal planes in all the zones, it follows that the (100), (010) spacings cannot "really" be halved, the disappearance of the Ist orders being due to the particular arrangement of the scattering centres with reference to those planes. The crystal must, therefore, belong to the space-group Q_h', the eight molecules (asymmetric) in the unit cell being arranged as in fig. 8 (B). Now there is a very simple structure which fulfils all these conditions.

The structural formula of succinimide may be written



the two OH groups of succinic acid having been replaced by one NH group.

According to the structure of succinic acid described above, the molecule is as shown in fig. 9.

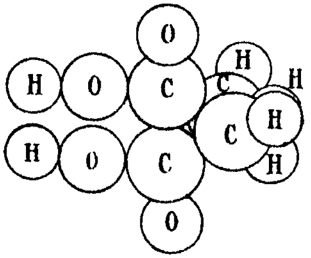


FIG. 9.

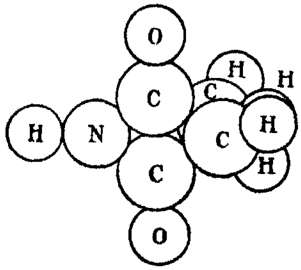
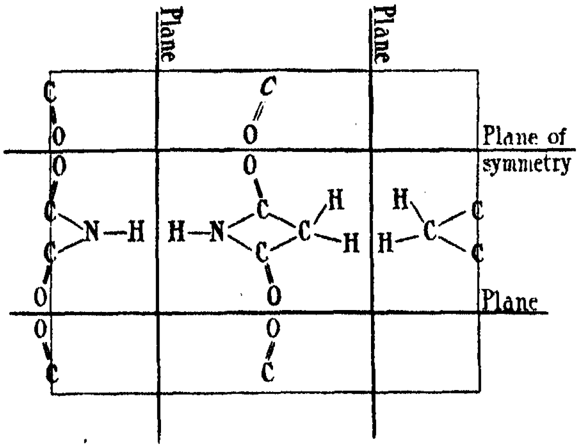


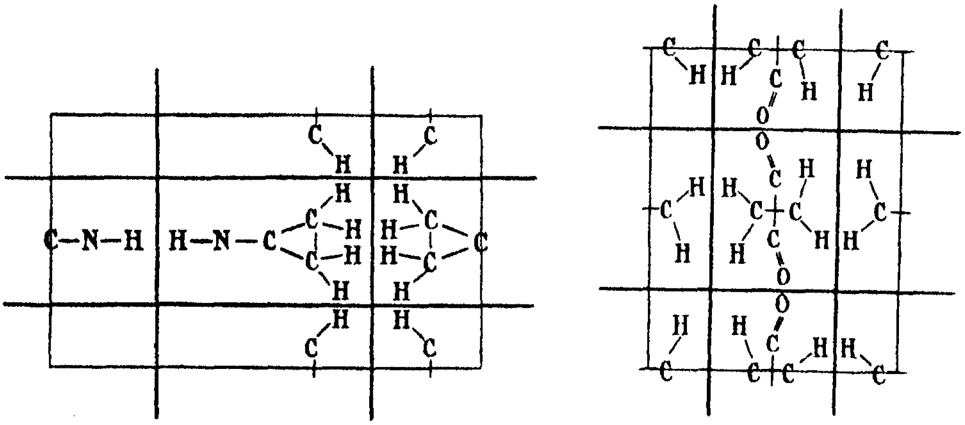
FIG. 10.

The molecule of succinimide obtained directly from this would be as shown in fig. 10, though possibly some slight rearrangement in the positions of the H atoms might take place, since these are, after all, only single nuclei.

Eight such molecules may very easily be fitted into the unit cell found, so that the completed structure has just the elements of symmetry of Q_h'. The diagrammatic arrangement of atoms is shown in fig. 11 (A), (B), (C).



(A) {100} plane.



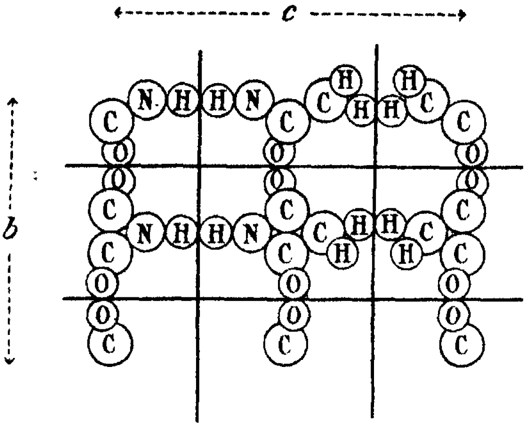
(B) {010} plane.

(C) {001} plane.

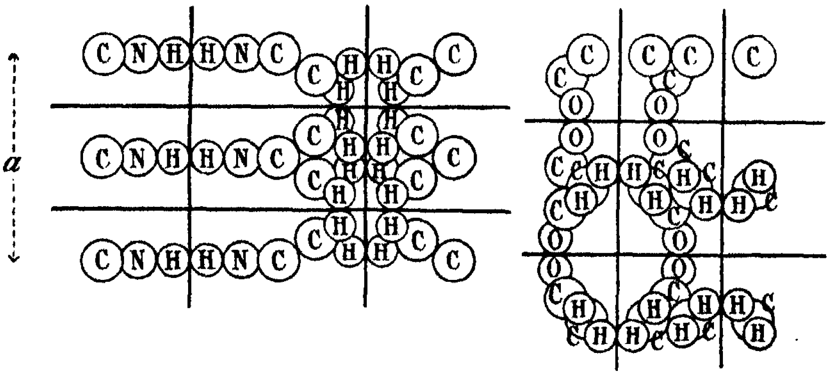
FIG. 11.

The actual projections of the crystal unit on the three axial planes would be as shown in fig. 12 (A), (B), (C).

Here, as in the case of succinic acid, the H atoms are too light to effect much scattering of X-rays, and therefore their positions cannot be fixed definitely. The obliquity of attachment of the ketonic oxygens has been slightly exaggerated so as to show the planes of symmetry more clearly. A glance at the above figure shows in a striking manner why the (100) and (010) spacings are apparently halved, whereas the (001) spacing is not halved, though the IInd and IVth order reflections are much larger than the Ist. Actually, none of them are "really" halved, in the sense previously defined. It looks, from the diagram,



(A) {100} plane.



(B) {010} plane.

(C) {001} plane.

Fig. 12.

as if the (001) should be a cleavage plane. An attempt is still being made to grow crystals large enough for this point to be tested.

According to the structure here suggested, the atomic dimensions in succinimide are :—

C diameter = 1·54 Å.U.
Ketonic O diameter = 1·15 Å.U.
H diameter = 1·15 Å.U.
N diameter = 1·35 Å.U.

A comparative study of the three crystals examined shows that although they are closely akin to each other chemically, there is very little likeness between the forms in which they crystallise. It is possible, but not certain, that the crystals of succinic anhydride and of succinimide may belong to the same space-group. The molecules in the crystal evidently retain much the same arrangement of the component atoms when one radical is replaced by another, but the molecular symmetry in the crystalline state is easily lost. With regard to the question as to why any particular substance should crystallise in any particular system or class, one can only say that an adequate solution of this fascinating problem seems as remote as ever.

In conclusion, I wish to thank Professor Sir William Bragg for the kind interest he has taken in this work, and for his helpful criticism, and I have also to acknowledge my indebtedness to the Scientific and Industrial Research Department for the grant enabling me to carry on this research.

Summary.

The monoclinic holohedral crystal of succinic acid is shown to possess two molecules per unit cell, and is based on the Bravais lattice Γ_m. Each of these molecules has a plane of symmetry, and they may be brought into coincidence with each other by a screw of angle 180° and translation $b/2$; thus the space-group to which the crystal belongs is C_{2h}^2. A probable structure is discussed in detail, an explanation of cleavage and twinning being offered.

The orthorhombic crystal of succinic anhydride is based on the lattice Γ_o and has four molecules per cell. It is shown that the X-ray method fails to determine the *class* to which the crystal belongs. The space-group is either C_{2v}' or Q_h', and the molecule is either asymmetric or possesses a plane of symmetry.

In the unit cell of the orthorhombic holohedral crystal of succinimide there are eight asymmetric molecules, the fundamental lattice being Γ_o. The space-group is proved to be Q_h', and details of a probable structure are given. A comparison of the molecules of succinic acid and of succinimide is made, and the atomic dimensions deduced from the structure are stated.

Experiments on the Emission of Electrons under the Influence of Chemical Action.

By MANFRED BROTHERTON, B.Sc., A.Inst.P., King's College, London.

(Communicated by Prof. O. W. Richardson, F.R.S.—Received December 20, 1923.)

Several investigators have claimed that electrons are emitted from metals under the influence of chemical action. It was shown by Haber and Just that drops of liquid cæsium or the liquid alloy of sodium and potassium emit electrons when acted on, at a low pressure, by a number of chemically active gases.

Prof. Richardson investigated the phenomena with a view to obtaining quantitative information. He determined the characteristic curve for the emission from drops of a liquid alloy of sodium and potassium when acted on, at a low pressure, by Cl_2, $COCl_2$ and H_2O. He also showed that the distribution of energy among the emitted electrons obeyed Maxwell's Law.*

These results were established only to the degree of accuracy permitted by the experimental conditions. The present work was undertaken, under the direction of Prof. Richardson, with the object of improving the experimental methods, extending the observations over a wider range of pressures and emissions, and, if possible, of accounting for the exceptional effects found in Prof. Richardson's earlier experiments, and described in the first edition of 'The Emission of Electrons from Hot Bodies,' p. 294.

Description of the Apparatus.

The apparatus is, with the exception of certain alterations and additions, which are here described, similar to that described in Prof. Richardson's paper. A diagram of the "testing vessel" is given on page 23 of that paper.

The applied potential was measured by means of a Weston double-range voltmeter, where the range required was not more than 15 volts, and accurate readings were necessary; for potentials greater than 15 volts a Weston voltmeter reading to 100 volts was substituted.

The current was measured, as in the previous work, by means of a quadrant electrometer, but, in addition, a method due to Townsend† was substituted for the ordinary time-deflection method of observation. This had the following advantages:—

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* 'Phil. Trans.,' A, vol. 222 (1921).

† Townsend, 'Phil. Mag.,' vol. 6, p. 598 (1903).

(1) The error arising from the potential acquired by the system is eliminated. This error may be very large where the applied potential is of the order of one volt or less.

(2) With a suitable capacity the current may be measured with accuracy over a considerably wider range than is possible with the time-deflection method of observation.

(3) As the spot does not leave its zero position, no time is lost between two observations, while the spot is settling down. Thus a series of observations may be taken in a much shorter time than in the time-deflection method. This was a very great advantage in the present work.

(4) If the capacity of the condenser is known, the current can be found at once from the equation $i = C\,dv/dt$ without knowing the capacity of the electrometer system.

The Active Gas.

The active gas was a pre-war specimen of $COCl_2$ by Kahlbaum. It was kept under pressure in a narrow glass tube sealed at one end and closed at the other by a tap.

The Alloy.

The alloy was a liquid mixture of sodium and potassium whose composition ranged from NaK to NaK_2. As it was not the object of the present work to study the phenomenon in relation to the composition of the alloy, no effort was made to ensure that the alloy should be of a given composition. It was found desirable to employ compositions containing a large percentage of potassium as these were the less viscous and therefore gave a more uniform stream of drops.

Control and Supply of the Active Gas.

The main difference between this and the previous work lies in the method of supplying the active gas to the alloy.

A steady electron emission will depend, in addition to a regular stream of drops, on having a steady uniform supply of active gas. To secure this was the initial object of the present work.

It seemed probable from Prof. Richardson's work that the active gas tends to be adsorbed by the glass walls of the apparatus. The initial attempts to obtain a uniform supply of active gas were based upon this supposition.

A quantity of $COCl_2$ was allowed to evaporate into a glass sphere which was packed with glass wool. The pressure of the gas introduced was measured by means of a "U" tube containing H_2SO_4. If the gas were adsorbed by the glass wool the sphere would act as a reservoir, supplying a small steady stream of gas to the testing vessel. The relation between the saturation current and the time was examined for various initial pressures in the sphere (*e.g.*, $\frac{1}{4}$, $\frac{1}{2}$ and 1 mm. H_2SO_4, etc.).

The effect diminished with time in a linear fashion, and the total variation in 60 minutes was only 60 or 70 per cent., as compared with the relatively enormous variation in the method adopted in the previous work. The effect was larger and more constant with the higher pressures, and died off comparatively rapidly with the lower pressures (*i.e.*, $< \frac{1}{2}$ mm. H_2SO_4).

It seemed questionable whether the greater uniformity of effect obtained in this case was due to the adsorption of the gas by the glass wool or to the larger mass of gas introduced into the apparatus. In order to test this point two spheres of equal volume, one of them containing glass wool and the other empty, were tried in turn. An examination of the variation of the effect with time showed that the glass wool made no appreciable difference.

It was concluded that at the higher pressures the greater uniformity of effect was due to the greater mass of gas present and not appreciably to the glass wool, and that although the glass wool does no doubt adsorb the gas to a small extent, it would require an enormous amount of it to produce a reasonably large and steady effect at these pressures.

It appeared, therefore, from these preliminary experiments that a sufficiently steady emission could be obtained by introducing into the apparatus a quantity of gas, the mass of which was very large when compared with the rate at which it was being consumed.

This was obtained, finally, by means of the arrangement given in fig. 1.

It consists essentially of four glass spheres of equal volume, a U-tube containing H_2SO_4, and the gas generator. The pressure of the gas let in is measured by means of a sheet of squared paper set up behind the U-tube.

The method of controlling the amount of gas admitted to the apparatus was as follows. The tap T is closed. By keeping T_1, T_2 and T_3 open or closed, the gas can be let in to one or more of the flasks. By this arrangement the pressure can be varied over a considerable range. Thus if (say) a pressure of $\frac{1}{4}$ mm. is desired, the tap T_1 is closed and the gas allowed to pass into the first flask so that the pressure is 1 mm. This is done by removing the liquid air and gently warming the tube with the hand. If now the tap T_4 is closed and T_1 T_2 T_3

are opened the gas will distribute over the four spheres to a pressure of $\frac{1}{4}$ mm. H_2SO_4. It may be allowed to pass to the testing vessel through either the capillary or the tap T.

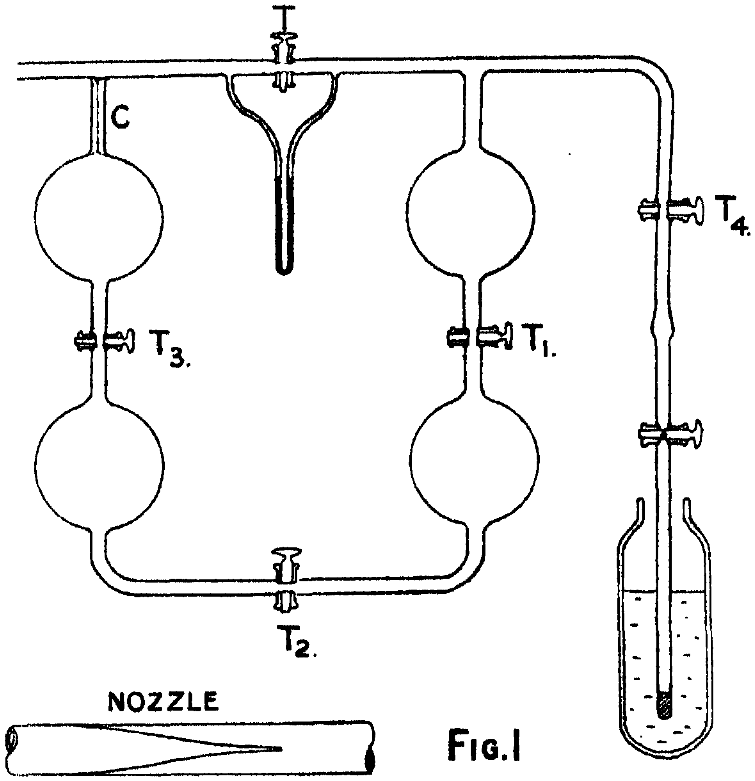

FIG. I

It appeared from an examination of the relation between the saturation current and the time that the former may increase or decrease or occasionally undergo a sudden and considerable change after having remained relatively constant. But, in general, after some initial fluctuation the saturation current settled down to increase or decrease in a gradual, linear fashion with time, for at least the first 60 minutes or so, and showed a tendency to remain constant or to increase at the higher pressures and to decrease at the lower pressures. Thus the emission remained sufficiently steady to obtain consistent observations, and during the experiments upon which the conclusions of this paper are based, the total variation in the saturation current was never more than 20 per cent. and usually less.

By means of the arrangement described above, it was possible to obtain initial pressures of $\frac{1}{6}$, $\frac{1}{8}$ and $\frac{1}{16}$ (mm. H_2SO_4), etc., but owing to the smallness of the mass of gas existing in the apparatus for these small initial pressures in the reservoir, the effect died off too rapidly to permit of reliable observations. Various obstacles, such as a plug of glass wool or a capillary tube, or both, were placed between the reservoir and the "testing vessel" with the object of impeding the flow of the gas from the reservoir, and so of obtaining a more constant and prolonged effect at low pressures, but these were not effective. In all cases the gas appeared to distribute itself more or less rapidly over the apparatus. It would be necessary to have a very large volume where the pressure is very small.

Subsequently the following device was introduced. The reservoir was filled, as in the other cases, and then continuously pumped out through an exceedingly fine glass nozzle (see fig. 1). With this device it was found possible to maintain a continuous and approximately steady stream of active gas at a very low pressure. The stream of gas was made to pass directly through the testing vessel so that it flowed through the copper cylinder in an axial direction. Under these conditions a stream of active gas was maintained in the neighbourhood of the drops and the gaseous reaction products were being continuously removed. The pressure in the remainder of the apparatus was, according to a McLeod gauge, less than 1/1000 mm., but the pressure in the neighbourhood of the drops was most probably higher than this.

This method gave remarkably consistent results and appears to be a very satisfactory one for studying the phenomena at low pressures. The saturation current increases or decreases in a gradual, linear fashion with time. In one experiment, for example, the saturation current rose only from $1 \cdot 10 \times 10^{-10}$ amps. to $1 \cdot 55 \times 10^{-10}$ amps. during a period of over two hours.

Experimental Procedure.

First Method, i.e., using the arrangement in fig. 1.—The gas was let into the reservoir to a given pressure (mm. H_2SO_4). The tap separating the reservoir from the rest of the apparatus was opened. After 10 minutes or so the pressure P_{10} was observed. The condenser was adjusted and the current measured for various accelerating potentials.

In Prof. Richardson's work, the saturation current (i_0) was measured before and after an observation (i), giving the quantity i/i_0. In the present work the saturation current was sufficiently constant to render this precaution unnecessary. Moreover, this method was undesirable for the following reasons:—

(1) If the saturation current is observed before and after an observation at a particular potential, a series of observations takes a considerably longer time and the saturation current may, meanwhile, alter by a large amount between the first and last observation.

(2) It tends to obscure certain important factors present in all the curves.

Although the effect was generally fairly uniform, increasing or decreasing slowly with time, it could not be relied upon to remain so. Occasionally, as described, the effect would vary considerably, in a haphazard manner, after having remained constant for a time. As a precaution, therefore, every curve was gone over twice, and as rapidly as possible, with increasing and then with decreasing potential or *vice versa*. If the two curves were similar, they were accepted as representing the true curve under the given conditions. In many cases, however, the series of observations had to be started over again, owing to a sudden variation in the effect. In other cases the effect was so variable that the apparatus was pumped out again and a new mass of gas let in.

Second Method, i.e., using the nozzle.—The reservoir was filled to a suitable pressure. The tap separating the reservoir from the nozzle was opened so that a steady stream of gas flowed into the testing vessel, whence it was continuously removed by the Gaede pump. After some initial fluctuations, the emission settled down to increase or to decrease steadily for hours, and there appears to have been no tendency to sudden fluctuations as in the other method, provided the speed of the pump and the rate of the drops remained constant. This was, in fact, the more reliable and satisfactory of the two methods.

The preliminary curves which were obtained by means of the first method were found, in general, to be different from those described by Prof. Richardson,* a considerably greater potential being required to produce saturation. It seemed probable that this discrepancy was due to the greater pressures prevailing. The emission was, accordingly, examined with a view to finding what effect, if any, the pressure of the active gas exerted on the characteristic curve.

The results obtained at low pressures will be described first. By varying the rate of the drops and the pressure in the reservoir a considerable range of saturation currents was obtained. The initial pressure in the reservoir was varied from ½ to 3/2 mm. H_2SO_4 and the rate of the drops from 1 in 11·1 secs. to 1 in 4 secs.; the saturation current ranged from $5 \cdot 7 \times 10^{-11}$ amps. to $6 \cdot 08 \times 10^{-8}$ amps. The composition of the alloy was also varied. In all cases a characteristic curve of the type given in fig. 2 was obtained, that is, it showed the following points:—

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* 'Phil. Trans.,' A, vol. 222 (1921).

1. The curve approached the voltage axis in the region of 1 volt.
2. Saturation invariably occurred within 3·5 volts and sometimes less.
3. The saturation part of the curve was parallel to the voltage axis up to 15 volts, beyond which it was not examined at low pressures.

By means of the first method the phenomenon was examined in relation to changes in the pressure of the active gas for fixed compositions of the alloy and approximately constant rates of the drops.

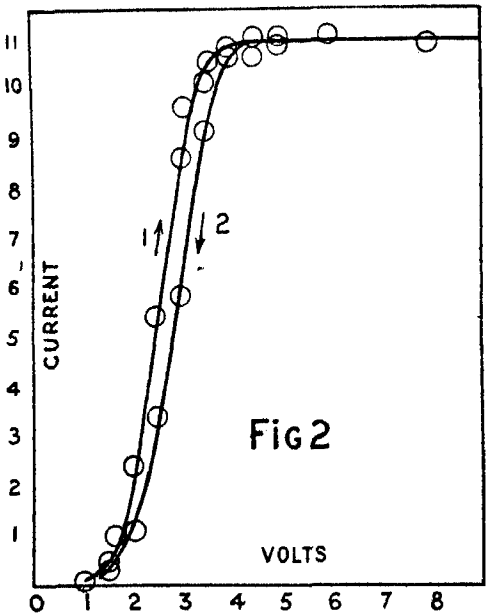


FIG 2

It must be remarked that one of the most uncertain factors in this work was the pressure existing in the apparatus. There were, in any case, no means of determining the pressure in the neighbourhood of the drops at a given time.

With the H_2SO_4 gauge, it was not possible accurately to measure the initial pressure of the gas admitted, firstly, because it was impossible accurately to read fractions of a millimetre, and, secondly, owing to the inevitable contamination of both the acid and the glass, the surface tension was affected, and the exact position of the meniscus rendered difficult to read.

It seems likely that the gas will distribute itself more or less rapidly over the apparatus; and it was assumed that when the emission had become steady, then the pressure had become uniform throughout. In general, the emission assumed a steady value within 10 minutes after the tap separating the reservoir from the rest of the apparatus had been opened. The pressure (denoted by P_{10}) was, therefore, read on the McLeod gauge 10 minutes after this tap had been opened, and may be accepted as a measure of the initial pressure of the active gas in the apparatus.

The observation P_F represents the reading on the McLeod gauge at the end of the experiment. This pressure will be partly due to the gaseous products of the reaction and to any occluded gas which may have come through with the alloy. The pressures P_{10} and P_F serve as a check on each other and as an indication of the pressure which has existed in the neighbourhood of the alloy during the experiment.

It was found that as the pressure of the active gas is increased the following changes occur:—

1. The saturation current increases.
2. The potential at which the smallest observation is taken increases, so that the curve has the appearance of moving bodily along the voltage axis.
3. The potential required to cause saturation increases.
4. The saturation part assumes an upward slope and turns upwards still more sharply after a certain potential.

These changes are clearly illustrated in figs. 3 to 7, which are typical of a large number of similar series obtained in the course of the work. The data are given below:—

No. of curve.	Initial pressure in reservoir (mm. H_2SO_4).	P_{10}.	P_F.	Rate of drops.	Added cap. (Mfd.)	Saturation current (amperes).
Fig. 3	0·5	8/1000	44/1000	1 in 10 secs.	0·05	$3{\cdot}05 \times 10^{-10}$
Fig. 4	0·75	15/1000	82/1000	1 in 11 ,,	0·20	$1{\cdot}1 \times 10^{-9}$
Fig. 5	1·0	19/1000	95/1000	1 in 10 ,,	0·40	$1{\cdot}8 \times 10^{-9}$
Fig. 6	1·5	44/1000	123/1000	1 in 9 ,,	0·45	$2{\cdot}25 \times 10^{-9}$
Fig. 7	2·0	125/1000	205/1000	1 in 13 ,,	0·50	unknown
Fig. 8	1·6	3/1000	10/1000	1 in 19·5 ,,	0·02	$1{\cdot}6 \times 10^{-10}$

It will be observed that the characteristic has changed by gradual stages from fig. 3, where the first observation is at 2 volts and the saturation part is parallel to the voltage axis, to fig. 7 where the smallest observation is at 9 volts and the saturation part has almost vanished, so that the characteristic has become very nearly a straight line up to 40 volts.

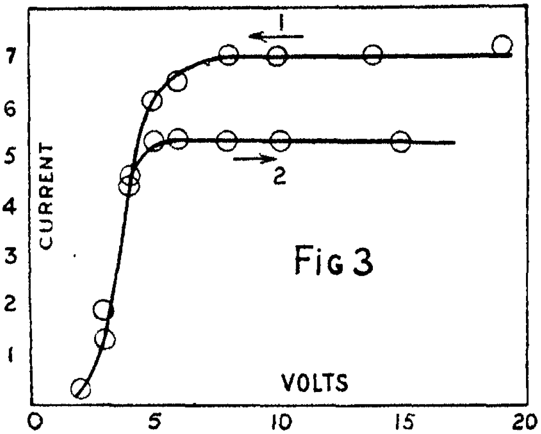


Fig 3

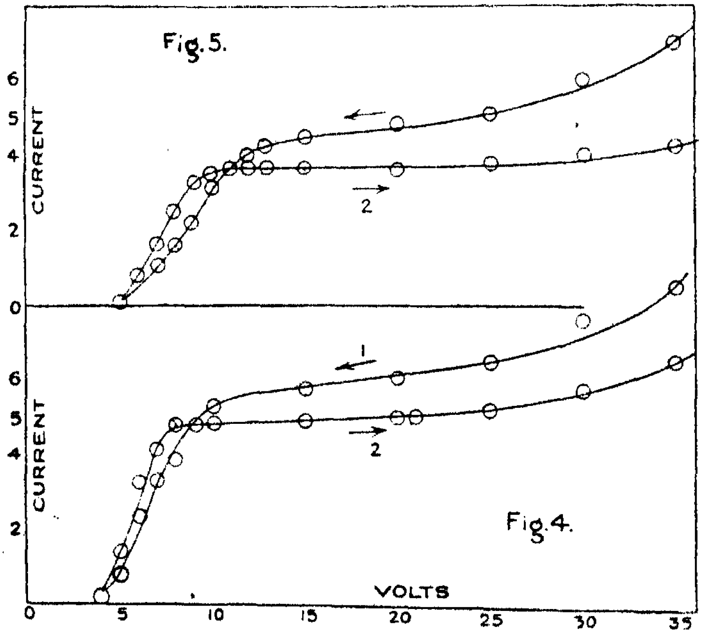
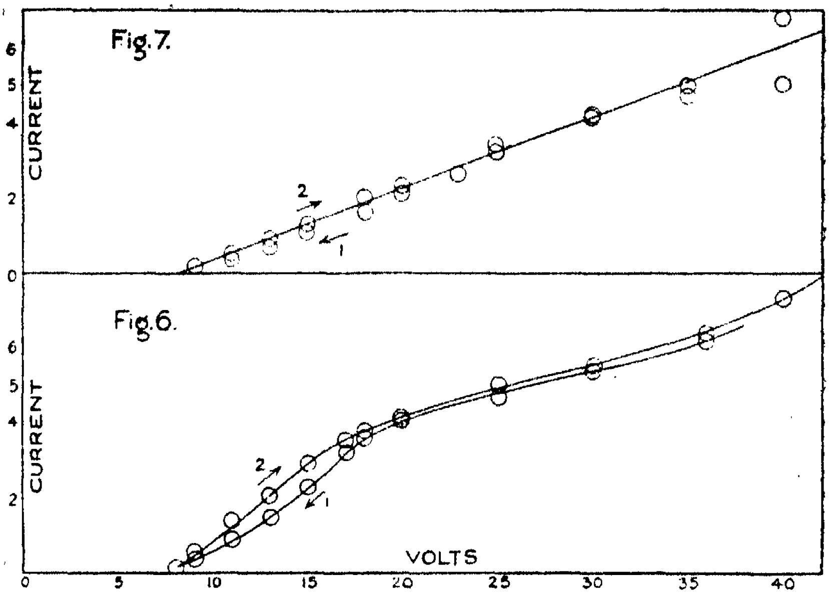


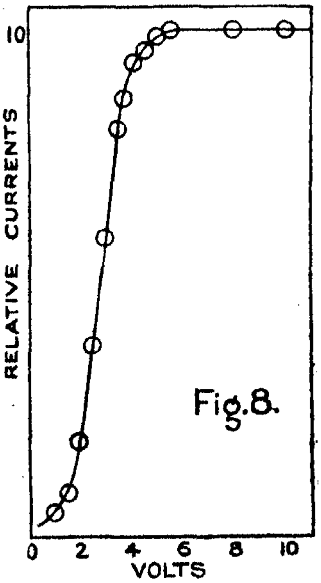
Fig. 5.

Fig. 4.

The numbers and arrows on the curves indicate the order and direction in which they have been taken. It will be observed that the magnitude of the



emission was decreasing throughout in figs. 4 and 5 and remained approximately constant in C (4 and 5), where the pressure, and therefore the mass of the active gas, was relatively large.



It must be pointed out that if the saturation current is diminishing with time and the observations are taken with decreasing potential, or vice versa, the saturation part will, in any case, exhibit an upward slope, so that the only satisfactory test of this point is to take the successive observations with increasing potential when the saturation current is diminishing with time, or vice versa. It follows that the upward tendency described above is more definitely established by the second curve than by the first in C (2 and 3).

In fig. 8, although the amount of gas let in was small, the saturation current; for some unknown reason, increased gradually throughout. The saturation current (i_0) was taken before and after an observation (i) at a given potential, and the ratio (i/i_0) is plotted against the potential. The points were remarkably consistent. This curve is included in order to illustrate a point repeatedly observed, namely, that there is no marked difference between different curves for the comparatively low pressures, although the latter may vary considerably. Thus, there is no great difference between figs. 2, 3, and 8; it is only for the relatively larger pressures and magnitudes of effect that the characteristic undergoes a marked change. The data of fig. 8 are given above.

In one group of experiments the alloy was very viscous and the drops slow and dull-looking. There may have been a slight air leak into the apparatus, introducing water-vapour, which would act on the drops without producing an emission comparable with that due to the $COCl_2$, and thus reducing the magnitude of the effect. So far as was observed, the effect was always smaller for viscous and dull-looking drops.

Owing, probably, to an accumulation of reaction products on the nozzle, the drops came through more and more slowly. The pressures are high and the magnitudes of the effects small. The shape of the curve was much the same in all cases, that is, the curve approached the voltage axis between 2 and 3 volts and saturated within a range of 4 volts, and the saturation part showed a slight upward tendency. Some data are given below.

No.	Initial pressure (mm. H_2SO_4).	P_F.	Rate of drops.	Added cap. (Mfd.)	Saturation current (amperes).
1	2·0	130/1000	1 in 14·75 secs.	0·10	$6 \cdot 5 \times 10^{-10}$
2	2·0	135/1000	1 in 22·70 „	0·01	$5 \cdot 0 \times 10^{-11}$
3	1.0	105/1000	1 in 26·75 „	0·01	$3 \cdot 5 \times 10^{-11}$
4	3·0	210/1000	1 in 35 „	0·01	$2 \cdot 0 \times 10^{-11}$

It will be noticed that the effect diminishes as the rate of the drops diminishes; thus, the saturation current is 30 times greater in 1 than in 4, although the pressure is considerably greater in the latter. It appears, therefore, that where the magnitude of the effect is small and the pressure high the pressure of the active gas has little, if any, influence on the shape of the characteristic.

In another case the alloy contained a high percentage of potassium and the nozzle was of a size such that the drops came through in rapid succession. The effects were, even at low pressures, very large compared with those obtained with much slower drops and high pressures. The effect appeared, in general, to be very erratic, probably owing to fluctuations in the rate of the drops.

With the higher pressures the total capacity of the condenser, *i.e.*, 3·0 mfd. was not sufficient to reduce the observations to reasonable proportions, so that the saturation current must have been greater than $4 \cdot 3 \times 10^{-8}$ amperes.

Where the rate of the drops was 54 per minute and the average pressure in the apparatus only 22/1000 mm., the saturation current was $3 \cdot 8 \times 10^{-10}$ amperes.

In all cases the curve approached the voltage axis somewhere beyond 10 volts. There is no obvious reason why this should happen. It may have been due to some unobserved error, but that would mean an error of 6 or 7 volts, which seems improbable. It must be remarked that the phenomena have not been thoroughly examined for rates of drops as large as the above.

A curious fact which was observed at all pressures and for all magnitudes of the emission was that the unsaturated part of the curve is steeper when the curve is taken with increasing potential than when it is taken with decreasing potential. This phenomenon is clearly evident in all the accompanying curves. It was equally apparent when the saturation current was increasing as when it was decreasing. The cause is not clear. It may be due to some space charge effect.

It seems likely that the basis factors determining the emission are :—

1. The amount of chemical action taking place in a given time. The drops form a layer of reaction products which is always more or less visible at the higher pressures, and it is probable, as Prof. Richardson has suggested,* that the electrons are prevented by this from leaving the drop, so that the potential required to cause saturation will depend to some extent on the thickness of the layer and thus upon the rate of the chemical action. This factor will in turn be dependent on the composition of the alloy, the rate of the drops, and the pressure of the active gas.
2. The presence of space charges.
3. The pressure of the gas apart from the chemical action it produces.

The approach of the characteristic to the voltage axis was investigated by Prof. Richardson and found to be gradual. The writer has examined the approach for a number of different pressures of active gas. In all cases it appeared to be asymptotic. In this respect the chemical characteristic is differentiated from the photoelectric curve and resembles the thermionic one. Up to the present, however, the data obtained are inadequate to lead to definite results. It is intended to deal with this point in a subsequent paper.

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* 'The Emission of Electrons from Hot Bodies,' p. 294.

Summary of Results.

The emission of electrons from liquid alloys of sodium and potassium when acted on by $COCl_2$ has been examined at both high and low pressures.

Two methods of supplying the active gas, at high and low pressures respectively, to the alloy have been devised which render it possible to secure an emission, varying by less than 20 per cent. in 60 minutes as compared with the comparatively enormous variation which occurred in the previous work.

The saturation currents ranged from $2 \cdot 0 \times 10^{-10}$ amperes to $4 \cdot 3 \times 10^{-8}$ amperes. The magnitude of the emission is dependent both on the rate of the drops and on the pressure of the active gas. The extent to which it is dependent on the rate and the condition of the drops is illustrated by the fact that the saturation current may be as large as $3 \cdot 8 \times 10^{-8}$ amperes where the rate of the drops is 54 per minute and the average pressure is only 27/1000 mm., and as small as $2 \cdot 0 \times 10^{-11}$ amperes where the rate of the drops is less than 2 per minute and the pressure as large as 210/1000 mm.

Since the phenomena have not been thoroughly examined for very slow or very fast rates of drops, an explanation of the exceptional results obtained under these conditions must be left until further information is obtained.

Apart from this the foregoing results appear to establish the following conclusions :—

1. The shape of the characteristic is dependent mainly on the pressure of the active gas, and independent of the composition of the alloy and the rate of the drops, at least at low pressures.

2. At low pressures the characteristic is represented by fig. 2. This is in agreement with the results given in Prof. Richardson's paper.

3. The changes illustrated in figs. 3, 4, 5, 6 and 7 are due, at any rate mainly, to changes in the pressure of the active gas.

It follows that a curve of the form given in fig. 4 will only be obtained when the amount of active gas present is comparatively large. This curve is similar to those obtained in Prof. Richardson's earlier experiments. It has been found, on examination of the data of these curves, that the pressure was comparatively large. The exceptional effects to which reference is made in the introduction are, therefore, satisfactorily explained.

The writer wishes to thank Prof. Richardson for many valuable suggestions in the course of the work.

Part of the cost of this work has been defrayed by a grant to Prof. Richardson from the Government Grant Committee of the Royal Society, which Prof. Richardson and the writer are glad to have this opportunity of acknowledging.

The Behaviour of Gases in Contact with Glass Surfaces.

By D. H. Bangham and F. P. Burt.

(Communicated by Prof. H. B. Dixon, F.R.S. Received November 23, 1923.)

(From the Chemistry Department, University of Manchester.)

That glass surfaces possess the property of taking up small quantities of gases is a fact of considerable interest to those engaged in accurate gas measurement. If, as seems probable, this property is closely connected with the " wetness " or " dryness " of the glass surface, the success of any quantitative experiments will depend on the constancy of the water content. Complete desiccation of glass may be impossible even at the melting-point, but Sherwood's experiments* indicate that glass which has been heated for a long time at a particular temperature loses very little further water on subsequent heating at or below that temperature.

In order to obtain a large surface, a quantity of fine glass wool was packed into a glass tube. The density of the material and the length per gram had been determined, so that the surface could be estimated. The wool was cleaned *in situ* with chromic and sulphuric acids, well washed with distilled water, and dried. After sealing to the apparatus the tube was electrically heated *in vacuo* for several days to a constant temperature in the neighbourhood of 200° C., the system being exposed to charcoal cooled in liquid air. The same treatment—but for a shorter time—was applied to the wool after each sorption experiment.

The apparatus is depicted in fig. 1. The gas was admitted through the tap J to the pipette A. After measurement it was distributed, by momentarily opening the tap C, to the exhausted wool tube B, which, together with the body of the pipette, was enclosed in an ice-bath. The residue of gas in the pipette was defined by the position of the mercury in the left-hand manometer D, while the rise of mercury in the right-hand manometer E marked the progress of the sorption. The tube G, dipping into the same trough F as the two manometers, served as a barometer in which the mercury was maintained at a constant needle-point setting by means of the screw-plunger M. Observations were made with the aid of an accurately graduated glass scale and a telescope provided with a Hilger micrometer eye-piece. An auxiliary telescope was used to control the point-setting of the barometer. Capillarity corrections were applied throughout.

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* 'J. Amer. Chem. Soc.,' vol. 40, 2, p. 1645 (1918).

The two systems A and B also communicated through a capillary tube sealed to taps J and K. This "short-circuit," which was provided with a small bulb L, came into operation when carrying out experiments near atmospheric pressure. In such cases the gas after measurement was condensed by immersing the bulb L in liquid air, and was afterwards evaporated through the tap K into the wool tube B. The whole apparatus, except the wool tube, was calibrated with mercury before being assembled. This enabled the volumes of gas in the different sections of the apparatus to be reduced separately to 0° C. from their observed temperatures.

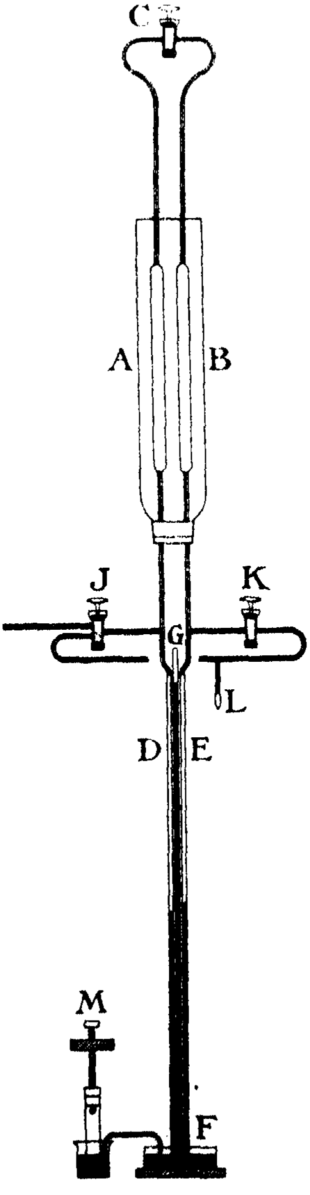

FIG. 1.

Elaborate precautions were taken to maintain at constant temperature the manometers and capillaries, since these parts of the system alone were not surrounded by ice. The dead-space volume of the wool tube was estimated by blank experiments with hydrogen, a very small correction (based on independent measurements) being applied for the sorption of this gas.

At the end of any sorption experiment the effect of a sudden reduction of pressure on the sorption-value could be estimated by exhausting the pipette and opening the tap C, whereby the pressure in the wool tube was approximately halved. This process could be repeated as often as was desired.

Experiments with carbon dioxide.

The gas obtained from a cylinder was dried over phosphoric oxide, solidified, exhausted, and finally sublimed *in vacuo.* Experiments were performed with this gas at pressures ranging from 6 mm. to 657 mm. In order that any fatigue effects (due to progressive removal of water or incomplete removal of gas) might have every chance of asserting themselves, the experiments were not performed in order of increasing or decreasing pressures, but in haphazard sequence. In spite of this, the sorption-values obtained at fixed times lie on smooth curves when plotted against the corresponding pressures, and, further, the two high-pressure experiments, although separated by an interval of 19 days (during which experiment 4 was carried out), led to practically identical results. Early readings were not taken in the case of these two experiments, since evaporation from the short-circuit bulb involved some uncertainty as to the exact time origin.

The following tables give the sorption values obtained at the times stated. Since the sorption of gas necessarily entailed a small diminution of pressure, the pressures at times of reading are also given. It will be noticed that the proportional fall of pressure was serious only when the initial pressure was very low.

Table I.—Experimental Results.

Exp. 1.—May 22, 1922.

Time (mins.)	p (mm. of Hg.)	s (c.c. at N.T.P.)
35·0	656·90	1·924
65·5	656·34	2·005
114·5	655·79	2·095
148	655·58	2·130
205	655·09	2·188
263	654·78	2·223
1410	652·04	2·503
2800	651·13	2·633

Exp. 2.—May 1, 1922.

Time (mins.)	p (mm. of Hg.)	s (c.c. at N.T.P.)
24·5	653·42	1·854
39·5	653·08	1·923
54·5	652·90	1·967
79·5	652·64	2·021
109·5	651·89	2·087
154·5	651·35	2·131
230	651·18	2·193
245	651·06	2·198
1310	648·92	2·476
1660	649·02	2·523
2840	648·02	2·621

Exp. 3.—March 11, 1922.

Time (mins.)	p (mm. of Hg.)	s. (c.c. at N.T.P.)
1·5	384·11	1·261
4·0	383·13	1·373
8·0	382·66	1·427
10·0	382·33	1·467
15·0	381·92	1·516
20·0	381·66	1·546
35·0	381·11	1·609
55·0	380·52	1·662
85·0	379·55	1·730
135	379·52	1·783
180	379·01	1·816
2850	375·29	2·239

Exp. 4.—May 8, 1922.

Time (mins.)	p (mm. of Hg.)	s (c.c. at N.T.P.)
1·0	346·31	1·176
4·0	345·20	1·295
7·0	344·65	1·353
10·0	344·39	1·384
15·0	343·96	1·430
30·0	343·21	1·512
60·0	342·44	1·592
90·0	341·82	1·641
145	341·28	1·690
220	340·73	1·744
1245	338·18	2·000

Table I—(continued).

Exp. 5.—March 23, 1922.

Time (mins.)	p (mm. of Hg.)	s (c.c. at N.T.P.)
1·3	231·52	0·999
4·0	230·55	1·092
7·0	229·99	1·146
11·0	229·62	1·181
16·0	229·27	1·215
35·0	228·38	1·300
85·0	227·32	1·402
160	226·62	1·470
345	225·65	1·568
1540	222·77	1·763

Exp. 6.—March 4, 1922.

Time (mins.)	p (mm. of Hg.)	s (c.c. at N.T.P.)
2·27	111·71	0·763
3·73	111·35	0·794
4·97	111·20	0·808
7·12	110·84	0·839
9·62	110·62	0·858
12·12	110·34	0·882
15·12	110·17	0·897
18·12	110·04	0·908
23·1	109·86	0·923
28·1	109·62	0·943
44·1	109·18	0·982
58·1	108·97	0·998
76·1	108·63	1·027
93·1	108·49	1·039
115	108·28	1·057
163	107·89	1·090
268	107·29	1·143
1373	104·96	1·308
2778	104·44	1·385

Exp. 7.—April 26, 1922.

Time (mins.)	p (mm. of Hg.)	s (c.c. at N.T.P.)
2·2	54·50	0·508
5·5	53·88	0·559
10·2	53·54	0·587
18·0	53·06	0·627
30·0	52·75	0·652
45·0	52·50	0·673
75·0	52·14	0·702
110	51·79	0·732
130	51·61	0·747
170	51·37	0·766
225	51·18	0·781
1310	49·40	0·927
2740	48·64	0·990

Exp. 8.—June 30, 1922.

Time (mins.)	p (mm. of Hg.)	s (c.c. at N.T.P.)
1·00	23·29	0·296
2·67	22·95	0·323
4·67	22·72	0·342
7·0	22·48	0·364
9·5	22·30	0·375
14·0	22·13	0·388
21·0	21·95	0·403
31·0	21·90	0·407
56·0	21·40	0·446
71·0	21·37	0·449
106	21·20	0·462
139	20·98	0·480
231	20·63	0·508
1290	19·49	0·598
2730	19·00	0·637

Exp. 9.—June 26, 1922.

Time (mins.)	p (mm. of Hg.)	s (c.c. at N.T.P.)
1·00	17·21	0·262
4·75	16·83	0·293
9·0	16·51	0·318
15·0	16·39	0·328
20·5	16·25	0·338
31·5	16·05	0·354
53·5	15·77	0·377
72·5	15·61	0·389
103·5	15·53	0·396
150	15·27	0·417
1260	14·06	0·512

Exp. 10.—June 19, 1922.

Time (mins.)	p (mm. of Hg.)	s (c.c. at N.T.P.)
1·50	6·19	0·150
4·75	6·01	0·164
10·75	5·81	0·179
17·75	5·73	0·186
37·75	5·55	0·199
101	5·23	0·224
175	5·17	0·229
355	4·96	0·245
1520	4·47	0·283
3040	4·24	0·302

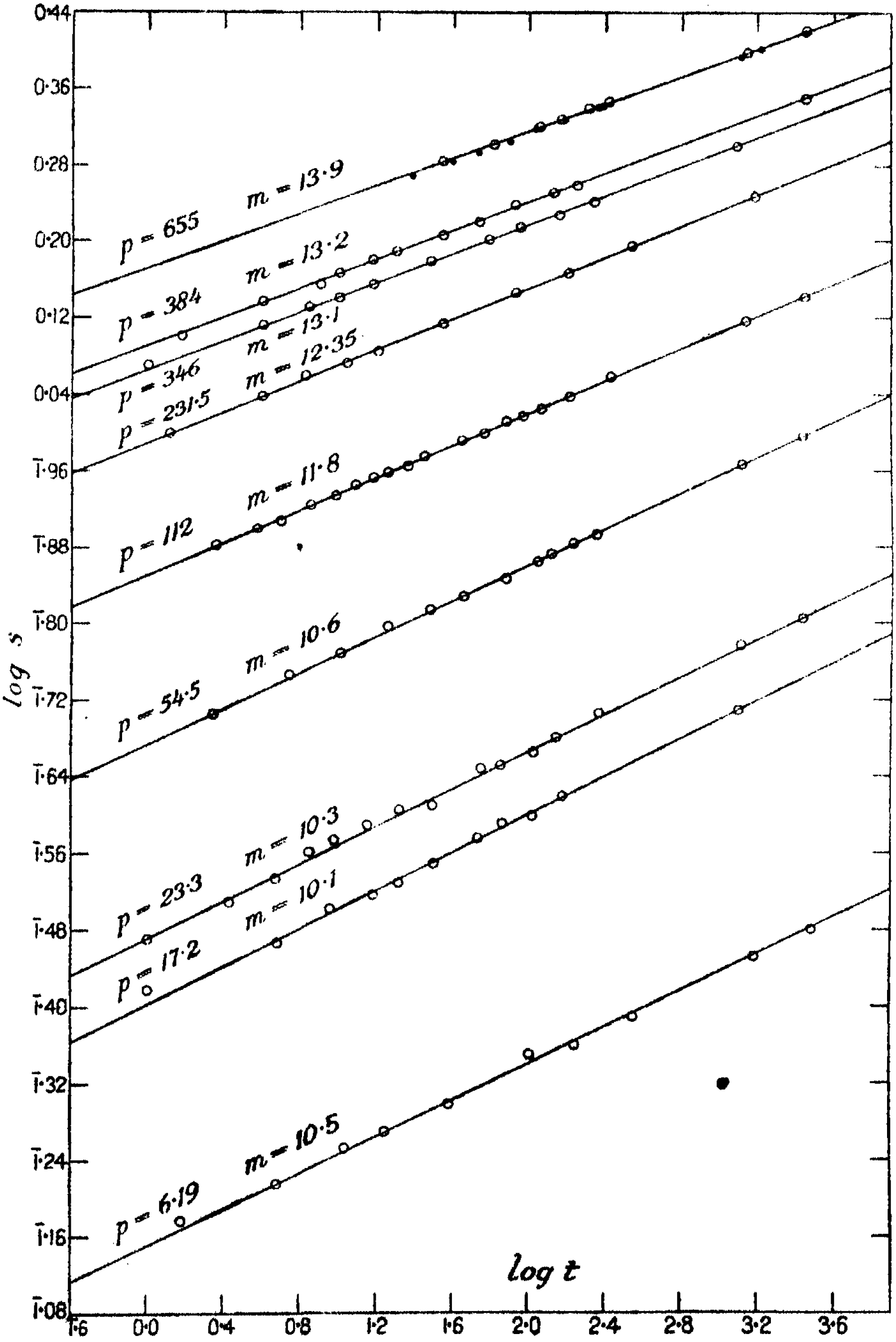
p = 655
m = 13·9
p = 384
m = 13·2
p = 346
m = 13·1
p = 231·5
m = 12·35
p = 112
m = 11·8
p = 54·5
m = 10·6
p = 23·3
m = 10·3
p = 17·2
m = 10·1
p = 6·19
m = 10·5
log s
log t
0·44
0·36
0·28
0·20
0·12
0·04
1̄·96
1̄·88
1̄·80
1̄·72
1̄·64
1̄·56
1̄·48
1̄·40
1̄·32
1̄·24
1̄·16
1̄·08
1̄·6
0·0
0·4
0·8
1·2
1·6
2·0
2·4
2·8
3·2
3·6

Fig. 2.

An examination of the data led to the conclusion that the results could not be interpreted by postulating a simple diffusion or solution process, since the rate of sorption ds/dt could not be expressed as the sum of any reasonable number of terms of the type ae^{-bt} (a and b being constants). When, however, the logarithms of the variables s and t were plotted, linear graphs were obtained in all cases (fig. 2).

This relation, which may be expressed in the form $s^m = kt$, since it implies that there is no upper limit to the amount of gas taken up, clearly indicates that the phenomenon under examination was the initial phase of an extremely protracted process. The index m in the above equation is a function of the pressure, having larger values at higher pressures. The high value of m in the 6 mm. experiment is undoubtedly due to the relatively large fall of pressure (30 per cent. of initial value) in this case. The above equation for the sorption process has met with very wide confirmation. Experiments with other gases (in the same wool tube) yielded very similar values for the index m.

Desorption Experiment.

At the end of experiment 3, by opening the tap C to the previously exhausted pipette, the pressure in the wool-tube was approximately halved. This was repeated at successive intervals of about 24 hours. It became clear that equilibrium is as difficult to reach from the desorption side as from that of increasing sorption. For short times after each pressure-reduction the quantities desorbed are fairly represented by the equation $r \log \zeta = \log t +$constant where ζ is the quantity desorbed in any given step at time t after the reduction

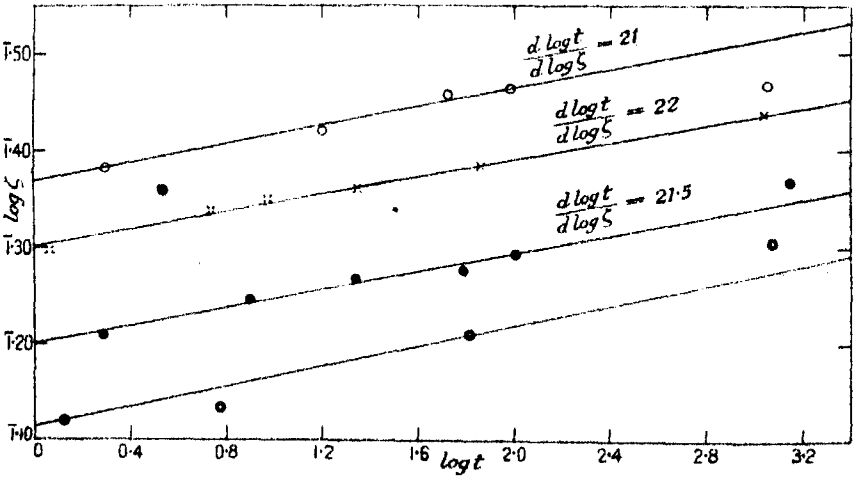

FIG. 3.

of pressure. This is illustrated in fig. 3. As ζ is very small, and necessarily measured with a falling meniscus, the results are somewhat irregular. The linear relationship has, however, been confirmed by extensive data obtained with other gases. It will be noticed that the last points on the different graphs lie below or above the straight lines drawn through the earlier points, according as gas was being sorbed or desorbed at the moment the last pressure reduction was made.

The quantities of gas remaining fixed about 24 hours after each pressure-reduction were found related to the corresponding pressures by the Freundlich equation $s^n = k'p$. Even if each desorption step had been considerably prolonged, the residual effect during such intervals (after the first 24 hours), while affecting appreciably the small quantity ζ, would represent a very small fraction indeed of the much larger quantity s. These considerations make it less surprising that the Freundlich equation should hold under conditions demonstrably removed from equilibrium. The following table contains the results of the desorption experiment with carbon dioxide, and of similar experiments with other gases.

Carbon dioxide ($n=4\cdot2$).			Nitrous oxide ($n=3\cdot2$).			Sulphur dioxide ($n=10\cdot7$).			Acetylene ($n=3\cdot7$).		
p (mm. of Hg.)	s obs. (c.c. at N.T.P.)	s calc.	p (mm. of Hg.)	s obs. (c.c. at N.T.P.)	s calc.	p (mm. of Hg.)	s obs. (c.c. at N.T.P.)	s calc.	p (mm. of Hg.)	s obs. (c.c. at N.T.P.)	s calc.
375·33	2·246	2·254	362·78	1·913	1·909	361·77	3·608	3·597	372·48	1·000	1·000
206·90	1·954	1·954	199·90	1·599	1·590	199·25	3·393	3·400	204·68	0·840	0·851
112·15	1·686	1·690	107·83	1·316	1·308	106·86	3·208	3·210	109·44	0·718	0·719
60·40	1·455	1·459	58·11	1·062	1·078	56·71	3·029	3·025	57·69	0·619	0·606
32·94	1·254	1·262	31·42	0·882	0·891	30·45	2·845	2·855	30·63	0·508	0·511
18·11	1·116	1·109	17·32	0·742	0·740	17·20	2·707	2·703	17·44	0·438	0·438
			9·86	0·627	0·621	10·07	2·577	2·573			

Under $s_{\text{calc.}}$ are given sorption values at the appropriate pressures read from straight lines drawn evenly through the experimental points obtained by plotting $\log s$ against $\log p$.

Experiments with ammonia led to sorption values much greater than for any of the above gases. While there appears to be a rough parallelism between the activity of the different gases and their solubility in water (great solubility being associated with high sorption-values and large values of the index n) there is certainly no direct proportionality between these two properties. In the case of all gases sorption-values were observed greatly exceeding those *required to form continuous films of monomolecular thickness on the surface as measured.*

We are anxious to express our great indebtedness to Mr. W. Sever, not only for the large amount of assistance which he gave us in the experimental work, but also for the many ingenious devices leading to increased accuracy and saving of time which he invented and made.

We wish also to acknowledge here the receipt of grants from the Royal Society Committee and from the Brunner Mond Research Fund, which partly defrayed the expenses of this investigation.

Optical Dispersion and Selective Reflection, with Application to Infra-red Natural Frequencies.

By T. H. Havelock, F.R.S.

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Introduction.

1. In a previous paper* I gave a comparison of the maxima of absorption and reflection as deduced from optical dispersion formulæ of various types. Exact equations, together with approximate solutions, were found for the maxima of κ and of $n\kappa$ and for the minima and maxima of n. The maximum of reflection was found by numerical and graphical methods in certain cases, both in the ultra-violet and in the infra-red; in particular, for rock-salt it was shown that available dispersion formulæ agreed in indicating a maximum of selective reflection at about 52μ, provided the formulæ were properly interpreted.

The infra-red frequencies of substances like rock-salt are of special interest in view of the various methods now available for estimating them from the point of view of crystal structure. The frequencies so calculated have generally been identified with the frequencies of the residual rays in the same region. For instance, Born†, using the dynamics of a simple crystal lattice, compared the natural wave-length with the maximum of selective reflection as given by residual rays; later, allowance was made for the difference between these wave-lengths, and an approximate formula given by Försterling* was used in making the correction.

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* 'Roy. Soc. Proc.,' A, vol. 86, p. 1 (1911).

† M. Born, 'Sitz. d. kgl. Preuss. Akad. d. Wiss.,' vol. 13, p. 604 (1918).

In the following paper I have extended the previous study of dispersion formulæ by obtaining an exact equation for the maximum of selective reflection in terms of the constants of the formula; in addition, a simple approximate solution of the equation is given. It appears, incidentally, that the approximate formula due to Försterling is incorrect. The results are applied in the first place to a study of various dispersion formulæ for rock-salt, sylvin and fluorspar. Further, assuming the data of crystal dynamics, some calculations are made to show to what extent the results affect the comparison between the resonance wave-length so obtained and the wave-length of residua rays.

Analysis of dispersion formula.

2. We shall use the generalised form

$$\frac{1}{\sigma + 1/(\mathbf{n}^2 - 1)} = \sum_s \frac{c_s}{p_s^2 - p^2 + ib_s p}, \tag{1}$$

where p is frequency, and $\mathbf{n}$ is the complex quantity $n(1-i\kappa)$. Well-known simple forms are obtained by taking $\sigma = 0$ or $\sigma = \frac{1}{3}$.

We are concerned here specially with the vicinity of some natural frequency p_s. The only assumption we make is that the region in question is sufficiently far removed from other similar regions that in the summation in (1) all the terms except one may be replaced by a quantity independent of p; so that we have for values of p near p_1,

$$\frac{1}{\sigma + 1/(\mathbf{n}^2 - 1)} = q_1 + \frac{c_1}{p_1^2 - p^2 + ib_1 p}. \tag{2}$$

After a little reduction, this gives on separating real and imaginary parts,

$$n^2(1-\kappa^2) = q_1' + \frac{c_1'(p_1'^2 - p^2)}{(p_1'^2 - p^2)^2 + b_1^2 p^2}; \quad 2n^2\kappa = \frac{c_1' b_1 p}{(p_1'^2 - p^2)^2 + b_1^2 p^2}; \tag{3}$$

in which

$$q_1' = \frac{1 + q_1(1-\sigma)}{1 - q_1\sigma}; \quad c_1' = \frac{c_1}{(1 - q_1\sigma)^2}; \quad p_1'^2 = p_1^2 - \frac{c_1\sigma}{1 - q_1\sigma}; \tag{4}$$

or, if we write

$$x^2 = q_1' p^2/c_1'; \; x'^2 = q_1' p_1'^2/c_1'; \; b^2 = q_1' b_1^2/c_1'; \; \alpha = x^2 - x'^2; \; \beta = bx; \tag{5}$$

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* K. Försterling, 'Ann. d. Phys.,' vol. 61, p. 577 (1920).

we have

$$\frac{n^2(1-\kappa^2)}{q_1'} = 1 - \frac{\alpha}{\alpha^2+\beta^2}; \quad \frac{2n^2\kappa}{q_1'} = \frac{\beta}{\alpha^2+\beta^2}. \tag{6}$$

It is convenient for comparison to use the same notation as before, and we put

$$g = \frac{1}{x'^2}; \; k = \frac{b}{x'}; \quad y = \frac{\alpha}{x'^2} = \frac{x^2-x'^2}{x'^2} = \frac{p^2-p_1'^2}{p_1'^2} = \frac{\lambda_1'^2-\lambda^2}{\lambda^2}. \tag{7}$$

Then on solving (6) we obtain

$$\frac{2n^2}{q_1'} = \left(1+\frac{g^2-2gy}{y^2+k^2y+k^2}\right)^{1/2} + 1 - \frac{gy}{y^2+k^2y+k^2}, \tag{8}$$

$$\frac{2n^2\kappa^2}{q_1'} = \left(1+\frac{g^2-2gy}{y^2+k^2y+k^2}\right)^{1/2} - 1 + \frac{gy}{y^2+k^2y+k^2}, \tag{9}$$

$$\kappa = \frac{\{(y^2+k^2y-gy+k^2)^2+g^2k^2(1+y)\}^{1/2}-(y^2+k^2y-gy+k^2)}{gk(1+y)^{1/2}}. \tag{10}$$

Finally, for reference, we express (3) in terms of wave-length, and in the same notation

$$\frac{n^2(1-\kappa^2)}{q_1'} = 1 + \frac{g\lambda^2(\lambda^2-\lambda_1'^2)}{(\lambda^2-\lambda_1'^2)^2+k^2\lambda_1'^2\lambda^2}; \quad \frac{2n^2\kappa}{q_1'} = \frac{gk\lambda_1'\lambda^3}{(\lambda^2-\lambda_1'^2)^2+k^2\lambda_1'^2\lambda^2}. \tag{11}$$

3. We may repeat briefly the previous results for the maxima of absorption. It was found that the maximum of the absorption index κ occurs at

$$y_\kappa = \tfrac{1}{6}[\{(4+k^2-g)^2+12(2g-k^2)\}^{1/2}-(4+k^2-g)], \tag{12}$$

with, under certain conditions, the approximate solution

$$y_\kappa = \tfrac{1}{2}g. \tag{13}$$

The equation for the maximum of $n\kappa$, which gives the position of maximum absorption, is

$$\begin{aligned} 12y^4 + (16+4k^2-8g)\,y^3 - (12g+8k^2+5gk^2)\,y^2 \\ - (4+g)(4+k^2)\,k^2y + (4g-4k^2-gk^2)\,k^2 = 0. \end{aligned} \tag{14}$$

It was shown that, in usual cases in practice, this equation has three roots with the following significance: the larger positive root (y_n) gives the minimum of n, the negative root ($y_{n'}$) the maximum of n, while the smaller positive root ($y_{n\kappa}$) gives the maximum of $n\kappa$. Approximate solutions which are fairly accurate, or at least indicate the first significant figure in the corresponding root of (14) are

$$y_n = \tfrac{1}{3}[\{(2-g)^2 + 9g\}^{1/2} - (2-g)], \tag{15}$$

$$y_{\kappa'} = -\frac{1}{6g}[\{(4+g)^2 k^4 + 12g^2k^2\}^{1/2} + (4+g)\,k^2], \tag{16}$$

$$y_{n\kappa} = \frac{1}{6g}[\{(4+g)^2 k^4 + 12g^2k^2\}^{1/2} - (4+g)\,k^2]. \tag{17}$$

4. We proceed now to the maximum of selective reflection. Assuming the external medium to be a vacuum, the reflective power is

$$\mathrm{R} = \frac{(n-1)^2 + n^2\kappa^2}{(n+1)^2 + n^2\kappa^2}. \tag{18}$$

This is a maximum when $\{n^2(1+\kappa^2)+1\}/n$ is a maximum; hence from (8) and (9) we require the maximum of

$$(q_1'\mathrm{A}^{1/2} + \mathrm{B}^{1/2})^2/\{(\mathrm{A}^{1/2}+\mathrm{B}^{1/2})^2 - g^2\}, \tag{19}$$

where

$$\mathrm{A} = y^2 + (k^2 - 2g)\,y + k^2; \qquad \mathrm{B} = y^2 + k^2y + k^2.$$

Differentiating (19) and substituting the values of $d\mathrm{A}$ and $d\mathrm{B}$ we get

$$\begin{aligned}(2y+k^2)\{q_1'\,(&\mathrm{B}^{1/2} - \mathrm{A}^{1/2} + \mathrm{A}^{-1/2}\mathrm{B} - \mathrm{AB}^{-1/2} - g^2\mathrm{A}^{-1/2})\\ &+ \mathrm{A}^{1/2} - \mathrm{B}^{1/2} + \mathrm{AB}^{-1/2} - \mathrm{A}^{-1/2}\mathrm{B} - g^2\mathrm{B}^{-1/2}\}\\ &\quad - 2g\,\{q_1'\,(\mathrm{B}^{1/2} + \mathrm{A}^{-1/2}\mathrm{B} - g^2\mathrm{A}^{-1/2}) - \mathrm{A}^{-1/2}\mathrm{B} - \mathrm{B}^{1/2}\} = 0.\end{aligned} \tag{20}$$

Using the value of B − A, a simple substitution leads to

$$\frac{q_1'\,(2y^2 - 4gy - 2gk^2 + 2g^2 - 2k^2) - 2y^2 + 2gy + gk^2 + 2k^2}{q_1'\,(-2y^2 + 2gy + gk^2 + 2k^2) + 2y^2 - 2k^2} = \frac{\mathrm{A}^{1/2}}{\mathrm{B}^{1/2}}. \tag{21}$$

We then form (A–B)/B and replace the values of A and B. Collecting finally the various terms, we obtain the following quartic equation in y.

$$\begin{aligned}12\,(q_1'-1)^2\,y^4 &- \{q_1'^2\,(24g - 16 - 4k^2) + q_1'\,(32 - 32g + 8k^2)\\ &\qquad + 8g - 16 - 4k^2\}\,y^3\\ &- \{q_1'^2\,(36g - 12g^2 + 15gk^2 + 8k^2) + q_1'\,(8g^2 - 48g - 20gk^2 - 16k^2)\\ &\qquad + 12g + 5gk^2 + 8k^2\}\,y^2\\ &- \{q_1'^2\,(-24g^2 + 12gk^2 - 6g^2k^2 + 16k^2 + 3gk^4 + 4k^4)\\ &\qquad + q_1'\,(16g^2 - 16gk^2 + 4g^2k^2 - 16k^2 - 4gk^4 - 8k^4) + 16k^2\\ &\qquad + 4gk^2 + gk^4 + 4k^4\}\,y\\ &- q_1'^2\,(4g^3 - 12gk^2 - 12g^2k^2 - g^3k^2 + 3gk^4 + 4k^4)\\ &\qquad - q_1'\,(16gk^2 + 8g^2k^2 - 4gk^4 - 8k^4) + 4gk^2 - gk^4 - 4k^4 = 0.\end{aligned} \tag{22}$$

Since $y = (\lambda_1'^2 - \lambda^2)/\lambda^2$, this gives the value of λ for maximum reflection, when the dispersion formula has been put into the form (11) for the region in question.

We notice, as a partial check, that in the limit when q_1' is small the process of finding the maximum of R is equivalent algebraically to finding the maximum of n; the equation (22) does, in fact, reduce to the previous equation (14) for $q_1' = 0$. In practice equation (22) is not so cumbersome as it appears. The quantity k is small, of the order $0 \cdot 1$, while q_1' and g are of the order 2; further the root required is the least positive root and is usually less than unity. In fact, the value of k, which introduces the absorption coefficient, does not affect much the position of the maximum of reflection, though, of course, it influences the amount of reflection. We shall find that we obtain a close approximation by using the simpler equation deduced from (22) by putting $k = 0$, namely,

$$\begin{aligned} 3(q_1' - 1)^2 y^4 - \{q_1'^2(6g - 4) + q_1'(8 - 8g) + 2g - 4\} y^3 \\ - \{q_1'^2(9g - 3g^2) + q_1'(-12g + 2g^2) + 3g\} y^2 \\ + (6q_1' - 4) g^2 q_1' y - g^3 q_1'^2 = 0. \qquad (23) \end{aligned}$$

Finally, in many cases a good approximation is obtained, which gives at least the first significant figure in the required root, by taking the last two terms of (23) and hence

$$y_R = \frac{g q_1'}{6q_1' - 4}. \qquad (24)$$

The corresponding wave-length is

$$\lambda_R = \frac{\lambda_1'}{\sqrt{\left(1 + \frac{g q_1'}{6q_1' - 4}\right)}} \qquad (25)$$

5. These results are easily generalised if the outer medium is not a vacuum, but is some transparent medium of refractive index n', as may be the case in experimental work. Since the reflective power is now

$$\frac{(n - n')^2 + n^2\kappa^2}{(n + n')^2 + n^2\kappa^2}, \qquad (26)$$

it follows that the previous work holds for the relative index n/n'. Thus the exact equation for the maximum of reflection is (22) with q_1' replaced by q_1'/n'^2; further, the approximate solution is

$$y_R = g q_1'/(6q_1' - 4n'^2), \qquad (27)$$

provided the relative magnitude of q_1'/n'^2 is suitable for this approximation.

6. For comparison we may put (25) into the notation used by Born, Försterling and other writers; with the dispersion formula as

$$n^2 = n_0^2 + \frac{K}{1 - \lambda_0^2/\lambda^2}, \tag{28}$$

we put in (25),

$$\lambda_1' = \lambda_0; \quad q_1' = n_0^2; \quad gq_1' = K. \tag{29}$$

Försterling, in the paper already quoted, gave the approximate formula

$$\lambda_R = \lambda_0/\{1 + K/2n_0^2\}^{1/2}, \tag{30}$$

which only agrees with (25) for $n_0^2 = 1$, whereas in most cases it is about 2 or 3. In his analysis Försterling makes two assumptions. One is the unusual method of introducing absorption into the dispersion formula, but this would not of itself affect much the approximate result. The other occurs in his treatment of the expression for the reflective power R, where in effect he takes n_0^2 to be unity in one part of the expression while retaining it in another part. The result of these assumptions is that the maximum for R is made to coincide with the maximum of the absorption index κ. In fact, if n_0^2 is put equal to unity, his expression (30) gives in our notation $y_R = \frac{1}{2}g$; and this is just the first approximation for the maximum of κ which we found in (13).

Comparison with experimental results.

7. The chief difficulty in comparing these formulæ with experimental values is in assigning a suitable value to the absorption coefficient; available estimates are generally for the visible or ultra-violet part of the spectrum. In the previous paper I examined the results for various liquids. For iodeosin in the region of absorption near $\lambda_1' = 5 \cdot 21 \times 10^{-5}$cm. the value of k was found to be $0 \cdot 1242$; and in applying the calculations to carbon disulphide, $0 \cdot 1$ was adopted as a suitable approximate value of k.

In some later experiments, Hulburt* has examined carefully various liquids and analysed the results in the manner suggested previously. Hulburt calculated the value of k from his determinations of reflective power. The simplest wave-length to use for this purpose is λ_1'; for there we have

$$2n^2 = q_1'(1 + g^2/k^2)^{1/4} + 1; \quad n^2(1 + \kappa^2) = q_1'(1 + g^2/k^2)^{1/2}. \tag{31}$$

From these we have the value of R in terms of q_1', g and k; and knowing R, q_1' and g we can deduce the value of k. For carbon disulphide, with $\lambda_1' = 2 \cdot 284 \times 10^{-5}$ cm., Hulburt found in this way $k = 0 \cdot 225$; while for monobromnaphthalene near $\lambda_1' = 2\cdot 29 \times 10^{-5}$ cm., $k = 0\cdot 135$. It is true that the calculated curves of reflective power in these cases show only tolerable agreement with experiment; but the discrepancies are ascribed, and no doubt correctly, to the existence of subsidiary regions of absorption near those which are examined. In other words, the simplification made in passing from (1) to (2) was not fully justified in these cases. As far as infra-red regions are concerned, there are not many suitable results available. Previously, I adopted for rock-salt the value $k = 0\cdot 1$ as sufficiently accurate for the purpose, and this was justified by the fact that it gave reflective powers of the right order; reference may be made to fig. 2 of the previous paper, showing a maximum reflective power of about $0\cdot 76$ at $52\,\mu$. Fortunately, as far as the position of maximum reflection is concerned, we shall see that any reasonable value of k, say between zero and $0\cdot 2$, gives a close enough approximation for comparison with experiment.

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* E. O. Hulburt, 'Astrophys. Journ.,' vol. 46, p. 1 (1917).

8. *Rock-salt, NaCl.*—The most accurate dispersion formula appears to be that due to Maclaurin,* who obtained it in the form

$$\frac{n^2-1}{n^2+a} = \frac{K-1}{K+a} + \frac{c_1}{\lambda^2-\lambda_1^2} + \frac{c_2}{\lambda^2-\lambda_2^2}, \tag{32}$$

$$\begin{aligned} a &= 5\cdot 51 \quad ; & K &= 5\cdot 9 \\ \lambda_1 &= 0\cdot 12652\,\mu \quad ; & \lambda_2 &= 51\cdot 3\,\mu \\ c_1 &= 0\cdot 00191605 \; ; & c_2 &= 683\cdot 816. \end{aligned}$$

This gives a close agreement over a large range of wave-length, from $0\cdot 486\,\mu$ to $22\cdot 3\,\mu$. In the infra-red near λ_2, the second term in (32) is quite inappreciable for our present purpose; then turning (32) into the form (11) for this region, we have

$$\frac{n^2}{q_1'} = 1 + \frac{g\lambda^2}{\lambda^2-\lambda_1'^2}, \tag{33}$$

$$q_1' = 2\cdot 332\,; \quad g = 1\cdot 53\,; \quad \lambda_1' = 61\cdot 9\,\mu\,;$$

where the suffix unity has been transferred to the infra-red. Assuming the coefficient of absorption to be such that $k = 0\cdot 1$, we substitute the values of q_1', g, and k in (22) and obtain the equation

$$21\cdot 29y^4 - 69\cdot 3y^3 - 38\cdot 3y^2 + 217\cdot 59y - 77\cdot 42 = 0. \tag{34}$$

The required root of this equation is $y = 0\cdot 4025$, which gives

$$\lambda_R = 52\cdot 3\,\mu. \tag{35}$$

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* R. S. Maclaurin, 'Roy. Soc. Proc.,' A, vol. 81, p. 367 (1908).

The position determined by residual rays is $52\,\mu$, which appears to be the mean of a double maximum. To show the relatively small effect of the value of k, we form the equation (23) in which $k = 0$; it is

$$21\cdot29y^4 - 69\cdot37y^3 - 37\cdot53y^2 + 218\cdot19y - 77\cdot92 = 0, \qquad (35\text{A})$$

and the root of this is $0\cdot4034$ or $\lambda_R = 52\cdot2\,\mu$.

Finally, the simple approximation (24) gives

$$y = gq_1'/(6q_1' - 4) = 0\cdot36; \quad \lambda_R = 53\cdot1\,\mu. \qquad (36)$$

Försterling's expression (30), which we have shown to be incorrect, would have given from the same data, $y = 0\cdot765$ or $\lambda_R = 46\cdot6\,\mu$.

Another formula of the same type as (32) has been put forward by Marvin,[*] and is of interest because it is accompanied by a similar formula for sylvin. The account of these is contained in a preliminary note, and the complete results do not appear to have been published; however, there is sufficient to enable us to deduce formulæ for the infra-red. Marvin uses two resonance wave-lengths in the ultra-violet, and gives for rock-salt, in the notation of (32),

$$a = 6; \quad K = 5\cdot92; \quad \lambda_1 = 0\cdot113\,\mu; \quad \lambda_2 = 0\cdot154\,\mu; \quad \lambda_3 = 51\cdot7\,\mu. \ (37)$$

The values of c_1, c_2 and c_3 are not given. For our purpose the first two may be neglected near λ_3, and c_3 may be found from a known value of n in the infra-red. For instance, taking the two values $n = 1\cdot3735$ at $20\cdot57\,\mu$ and $n = 1\cdot3403$ at $22\cdot3\,\mu$, we find the values $675\cdot74$ and $675\cdot70$ respectively for c_3. Taking the mean value, and transforming to the form (33), we find

$$q_1' = 2\cdot333; \quad g = 1\cdot53; \quad \lambda_1' = 61\cdot8\,\mu. \qquad (38)$$

This, as might be expected, is practically the same as from Maclaurin's formula and leads to the same value of λ_R. Paschen's[†] formula for rock-salt is of the simpler form in which the quantity σ is taken as zero; taking his formula and putting it into the same form (33) for the infra-red, we find

$$q_1' = 2\cdot33; \quad g = 1\cdot44; \quad \lambda_1' = 60\,\mu. \qquad (39)$$

This, by the approximate formula (25), gives $\lambda_R = 51\,\mu$. Reviewing these calculations we may say that the various dispersion formulæ, though given in different forms for the whole range, agree in indicating in the infra-red a maximum of selective reflection at about $52\,\mu$. We notice incidentally that Maclaurin identified the wave-length $51\cdot3$ in his formula (32) with the residual rays. We have seen that in changing to the form (33) this "resonance" wave-length is increased to $61 \cdot 9\,\mu$, and this leads to maximum reflection at $52 \cdot 3\,\mu$; it is an accidental coincidence due to the values of the constants that the last wave-length is near the first.

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[*] H. H. Marvin, 'Phys. Rev.,' vol. 17, p. 412 (1921).

[†] F. Paschen, 'Ann. der Phys.,' vol. 26, p. 130 (1908).

9. *Sylvin, KCl.*—Here we take the dispersion formula suggested by Marvin as analogous to that for rock-salt, namely, as in (37) but with

$$a = 6\,; \quad \mathrm{K} = 4 \cdot 85\,; \quad \lambda_1 = 0 \cdot 118\,\mu\,; \quad \lambda_2 = 0 \cdot 159\,\mu\,; \quad \lambda_3 = 61 \cdot 6\,\mu. \tag{40}$$

This gives for the infra-red

$$\frac{n^2 - 1}{n^2 + 6} = 0 \cdot 35484 + \frac{\mathrm{B}}{\lambda^2 - 3794 \cdot 56}. \tag{41}$$

Determining B from the data $n = 1 \cdot 3882$ at $20 \cdot 6\,\mu$ and $n = 1 \cdot 369$ at $22 \cdot 5\,\mu$, we find the mean value $801 \cdot 76$. Making the change into the form (33) we obtain

$$q_1' = 2 \cdot 1732\,; \quad g = 1 \cdot 232\,; \quad \lambda_1' = 71\,\mu. \tag{42}$$

After having shown in the previous section the degree of accuracy of the approximation, it is sufficient now to use the expression (27), and this gives

$$\lambda_{\mathrm{R}} = 62 \cdot 3\,\mu, \tag{43}$$

which is to be compared with $63 \cdot 4\,\mu$ from residual rays.

10. *Fluorspar, CaF$_2$.*—In this case Maclaurin has given a dispersion formula of the type (32) with

$$\left.\begin{array}{ll} a = 1 \cdot 04 \quad ; & \mathrm{K} = 6 \cdot 8 \\ \lambda_1 = 0 \cdot 08466 \quad ; & \lambda_2 = 24 \cdot 0074 \\ c_1 = 0 \cdot 001303\,; & c_2 = 231 \cdot 856. \end{array}\right\} \tag{44}$$

A similar reduction to (33) gives

$$q_1' = 2 \cdot 039\,; \quad g = 2 \cdot 3345\,; \quad \lambda_1' = 38 \cdot 3. \tag{45}$$

In view of the larger value of g than in the previous cases, we use first the more accurate equation (22) with $k = 0 \cdot 1$, or

$$12 \cdot 922 y^4 - 81 \cdot 94 y^3 + 33 \cdot 61 y^2 + 366 \cdot 2 y - 209 \cdot 18 = 0.$$

The root of this is $y = 0 \cdot 580$. The approximate solution (24) gives the value $0 \cdot 578$; and these give

$$\lambda_{\mathrm{R}} = 30 \cdot 5\,\mu. \tag{46}$$

The comparison with residual rays is interesting in this case, because Rubens gives two wave-lengths, namely, $24\,\mu$ and $31 \cdot 6\,\mu$. In the deductions which have been made from a simple theory of crystal structure, only one infra-red frequency is indicated in this region, and it is supposed to correspond to the longer wave-length $31 \cdot 6\,\mu$. On the other hand, Maclaurin was under the impression that in his form of the optical dispersion formula the wave-length given there in the infra-red was the smaller wave-length $24\,\mu$ of the residual rays. It is somewhat curious that, as we have shown, the formula really indicates a maximum of selective reflection at $30 \cdot 5\,\mu$ near the longer residual rays.

Data from crystal structure.

11. Natural frequencies in the infra-red of the class we have been considering have been calculated from various approximate formulæ from the theory of crystal lattices, and have been compared with the similar optical frequencies. It is not our purpose to discuss these methods here, but simply to take the data and to apply the suitable correction. It is convenient to refer to Born's* recent account of the subject, where detailed references will be found.

In the first place, we may notice the formula

$$\lambda_0 = \mathrm{C}\alpha^{1/2}\mathrm{M}^{1/3}\rho^{1/6}, \tag{47}$$

where C is assumed constant for crystals of similar structure, α is compressibility, ρ density, and M is derived from the atomic weights of the ions by $\mathrm{M} = (\mathrm{M}_1\mathrm{M}_2)^{3/2}/(\mathrm{M}_1 + \mathrm{M}_2)^2$. The constant C was determined empirically by making the formula give $\lambda_0 = 52\,\mu$ for rock-salt, so as to agree with residual rays; this gave $\mathrm{C} = 1 \cdot 177 \times 10^3$ sec.$^{-1}$.

But it would seem more correct to identify λ_0 with the natural wave-length in the dispersion formula when the latter has been put in the simple form (28), to use Born's notation; the comparison of residual rays with λ_{R} can then be made in each case.

Keeping rock-salt as the standard, we make $\lambda_0 = 61 \cdot 9\,\mu$ in accordance with (33); this gives $\mathrm{C} = 1 \cdot 4 \times 10^3$ sec^{-1}. Using the data given by Born (*loc. cit.*, p. 625), his table of results now becomes the following :—

Substance.	λ_0.	λ_{R} calc.	λ_{R} obs.
NaCl	61·9	52·2	52·0
KCl	72·6	63·4	63·4
KBr	94·6	—	82·6
KI	114·8	—	94·1
$\mathrm{CaF_2}$	39·9	31·7	31·6

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[*] M. Born, "Atomtheorie d. fest. Zustandes," 'Encyk. d. Math. Wiss.,' vol. 5. 3, Heft 4 (1923).

In this table λ_0 is found from (47) with NaCl as the standard. In the third column, λ_R has been calculated from (25), in the notation (29); while in the last column are the residual rays.

It may be noticed that for sylvin the value 72·6 is higher than the wave-length 71 μ of (42). The corresponding values of n_0^2 and K of the formula (28) were found by making (28) give the correct values of n at $\lambda = 20 \cdot 6$ and $\lambda = 22 \cdot 5$; the values so found were $n_0^2 = 2 \cdot 1749$, $K = 2 \cdot 8304$, and these were used in the calculation of λ_R. Similar calculations were made for fluor-spar, but there do not seem to be reliable values of the dispersion of KBr and KI in the infra-red to allow the same comparison to be made.

12. We consider now the work to which reference was made in the first section; the first four columns in the following table give the data as used by Born (*loc. cit.*, p. 629).

Substance.	n_0^2.	K.	λ_0.	λ_R calc.	λ_R obs.
NaCl	2·44	3·51	66·7	57·8	52·0
KCl	2·14	2·59	78·0	68·6	63·4
KBr	2·31	2·30	94·0	84·7	82·6
KI	2·67	2·44	115	105	94·1
CaF_2	2·02	4·79	53·1	42·1	31·6
ZnS	1·49	6·50	53·5	35·2	30·9
AgCl	4·07	6·85	127	110	81·5
AgBr	4·61	7·48	183	160	112·7

We may remark that the values of n_0^2 and K for rock-salt, sylvin and fluor-spar agree moderately well with the corresponding quantities q_1' and gq_1' we obtained in §§ 8-10; but these values of n_0^2 and K when used with the corresponding value of λ_0 given by Born would not give correct values of n from the dispersion formula (28). However, accepting the data, we calculate the wave-length λ_R from the formula

$$\lambda_R = \lambda_0 / \sqrt{\{1 + K/(6n_0^2 - 4)\}}.$$

The values so obtained are given in the fifth column of the above table, and the last column gives the residual rays.

We notice finally the calculations made from the point of view of electrostatic cohesion (Born, *loc. cit.*, p. 741); the data are given in the first four columns of the following table :—

Substance.	n_0^2.	K.	λ_0.	λ_R calc.
NaCl	2·83	2·99	61·6	55·5
KCl	2·40	2·35	74·5	67·3
KBr	2·68	1·98	88·0	81·5
KI	2·95	2·15	108·3	100·8

Here the values of n_0^2 and K do not agree very well with those found from optical dispersion; but using these values, the last column gives the values of λ_R. Both in this table and in the preceding one, the new calculated values of λ_R show a less favourable agreement with the residual rays than those given by Born. The approximate formulæ derived from theories of crystal structure are of great interest, but one cannot expect as yet more than approximate agreement with experimental values. The purpose of the preceding calculations is to show the necessity for using in these comparisons a proper correction for the difference between λ_0 of the dispersion formula and λ_R the maximum of selective reflection.

On the Determination of the Crystal-Axes in "Single-Crystal" Aluminium Bars by Means of X-Rays.

By ALEX MÜLLER.*

(Communicated by Prof. Sir E. Rutherford, F.R.S.—Received February 25, 1924.)

[PLATE 4.]

Introduction.

Mr. G. I. Taylor, F.R.S., and Miss C. F. Elam* investigated recently the distortion of "single-crystal" aluminium bars during a tensile test. By purely geometrical measurements they found that certain planes exist in the test-piece which, during its extension, remain undistorted. That is to say, that any curve drawn on these planes keeps its shape. From these observations they concluded that the test-piece must have a lattice-structure extending through the bulk of the material, or, in other words, that these test-pieces are single crystals.

Mr. Taylor asked the writer to investigate by means of X-rays whether the "undistorted" or slip-planes could be related with the crystal-planes of the material which is known to crystallize in a face-centered cubic lattice. The result of this investigation is given in the above-mentioned paper of Taylor and Elam. The present paper is meant to give an account of the experiments so far as the X-ray work is concerned. A few points will be discussed later on which are likely to be of a more general interest.

Statement of the Problem.

From their measurements Taylor and Elam were able to give the position of the slip-planes relative to a fixed plane in the specimen. This plane will be called the reference plane. The X-ray problem was to do the same thing for the crystal planes; that is to say, to find the position of the lattice planes of the crystal relative to the same reference plane.

Description of the System of Co-ordinates and of the Reference Plane.

The samples under test were bars of a square or circular cross-section. They are fully described in Taylor and Elam's paper. The reference plane for the square bar was one of its boundary surfaces. The corresponding plane in the round bar was defined by a pair of parallel scratches, *aa* and *bb*, on the surface, drawn through opposite points of the diameter of the cross-section. (Fig. 1.)

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* Taylor and Elam, 'Roy. Soc. Proc.,' A, vol. 102, p. 643 (1923).

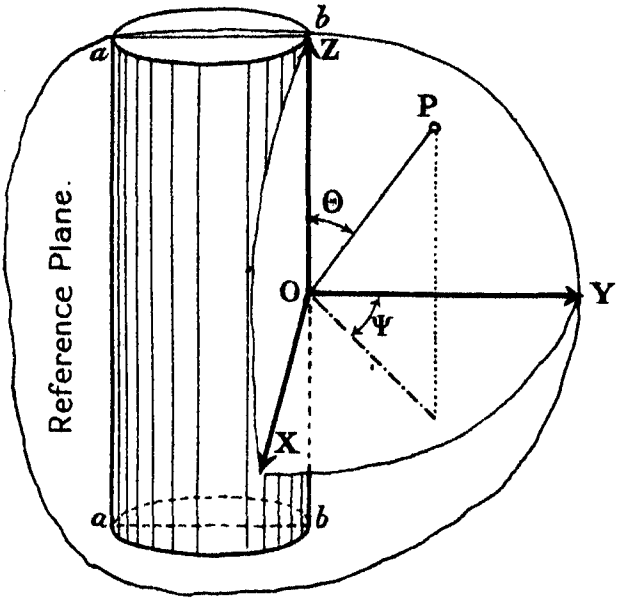


Fig. 1.

The position of the lattice relative to the reference plane was given in angular co-ordinates as follows :—Let X, Y, Z be the axes of a rectangular system of co-ordinates. The X axis is perpendicular to the reference plane, the Y axis in the reference plane and the Z axis in the reference plane, and parallel to the length-axis of the bar (fig. 1). The direction of a line OP is then defined by the two angles θ and ψ. The position of our cubic lattice is completely described in our system of co-ordinates if we know θ and ψ for the normals of two crystal planes, the indices of which we know.

The way the values of the two sets of θ and ψ were found will now be described.

Geometrical Optics of the Spectrometer and Description of the Experiments.

The test-piece was fixed on the table of a small spectrometer in such a way that its axis was parallel to the axis of rotation of the spectrometer-table. By a suitable adjustment one of the surface markings could be made to coincide with this axis. A cylindrical beam of homogeneous X-rays from a copper anticathode, the path of which was perpendicular to the axis of the spectrometer, struck the surface of the aluminium bar in a point O (fig. 2). A photographic plate was placed in a holder behind the test-piece. The incident beam was perpendicular to the plate surface. The plate-holder could be shifted up and down, parallel to the spectrometer axis, and in such a way that the plate surface remained always at the same distance from O. It will be shown later that it was necessary to measure the angle between the incident X-ray beam and the reference plane. This was done in the following way :—A small microscope, the axis of which was at right angles to the spectrometer axis and at right angles to the incident beam, could slide in V-grooves which were rigidly connected with the spectrometer. The only motion the microscope could perform was a displacement parallel to its own axis. By turning the spectrometer table the image of the surface markings could be brought into coincidence with the cross-wires of the microscope. In this position, when the reference plane was at right angles to the incident beam, the zero-reading was taken on the spectrometer scale. Any other setting angle between the incident beam and the reference plane could now be obtained by turning the spectrometer table through the necessary angle from the zero-position. The spectrometer scale was divided in degrees : 1/10° could be read on the vernier. The specimen could be moved parallel to itself by means of a mechanical stage fixed to the spectrometer.

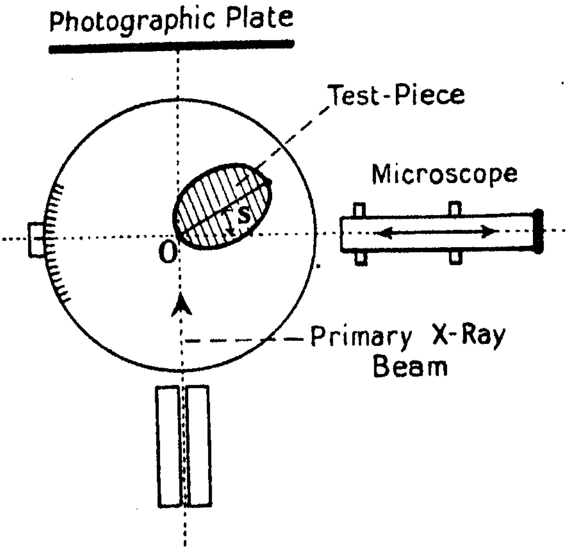


Fig. 2.

The photographs were taken in the following manner:—A short exposure was given with the spectrometer table set in the zero-position. In this position the test-piece on the table covered only half of the cross-section of the incident beam, which therefore produced a centre-spot on the plate. The spectrometer table was then turned through a small angle, say 5°, and an exposure of between 5 and 10 min. was given. The table was then turned back to the zero-position and the exposure of the centre-spot was repeated. After the first exposure the photographic plate was moved through a small distance in its vertical slide. The result of this was that the centre-spots in the first and the second exposure were separated on the plate. This scheme was now continued; that is to say, the setting angle was increased by the same amount after each exposure and the plate was moved through the same small distance after the centre-spot had been taken. This gave a series of centre-spots on the plate, all arranged in a straight line, and each centre-spot corresponded to a known setting angle. In most of the experiments a setting angle was soon found for which X-ray reflection occurred. Reflections showed on the plate as short, dark lines or small spots. When a reflection had been found the experiment was repeated with a series of setting angles differing by only one, or at most, two degrees.

The question then arose as to how to identify the reflection-plane and find the centre spot on the plate to which the reflection belonged. This was very easily done. Aluminium gives strong reflections from the 111 and the 200 planes. It was found that only these two reflections appeared on the plates. From the known reflecting angles, called ϕ_{111} and ϕ_{200} in this paper, and from the measured distance between the axis of the spectrometer and the plate, it was easy to calculate the distance between a centre spot and a spot produced by the 111 or 200 reflection. By drawing circles with these two calculated distances as radii, and with a reflected spot as a centre, it was easy to find the centre spot to which the reflection belonged. In doubtful cases it was necessary to increase the distances between the centre spots. When the steps by which the setting angles were increased were sufficiently small, reflection occurred over a certain range of setting angles. This was partly due to the fact that the incident beam had a certain angular width and partly due to imperfections in the crystal, which often became very marked as the extension of the test-piece increased. The divergence of the primary beam was measured in a separate experiment. Care was taken that, when looking for reflections, the differences between the setting angles were small enough to be covered by the divergence of the primary beam. In doing this it was impossible to miss a reflection which would occur within the total range of setting angles investigated. Plate 4 shows a few typical photographs. In some of those reproduced two sets of setting angles are alternated; this is merely a matter of convenience. Thus in the third photograph from the left in the top row (Plate 4) the settings are from top to bottom 7°, 16°, 8°, 18°, 9°, 20°. It will be seen that there is a strong 200 reflection at 8°, but there are none at 7° or 9°. There are also reflections at 18° and 20°, but not at 16° or as was found from another plate, at 22°.

The reflecting angle ϕ and the setting angle s are not sufficient for calculating θ and ψ. A third angle, w, is required, which can be measured on the photographic plate (fig. 3). The figure represents a drawing made from an original plate; w is the angle between two planes. One plane is given by the primary beam and the axis of the spectrometer; the other plane is defined by the primary beam and the normal to the reflecting plane.

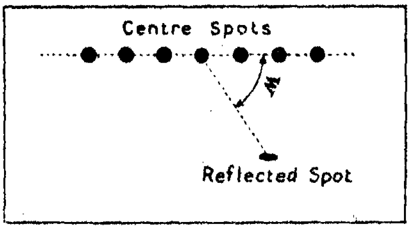


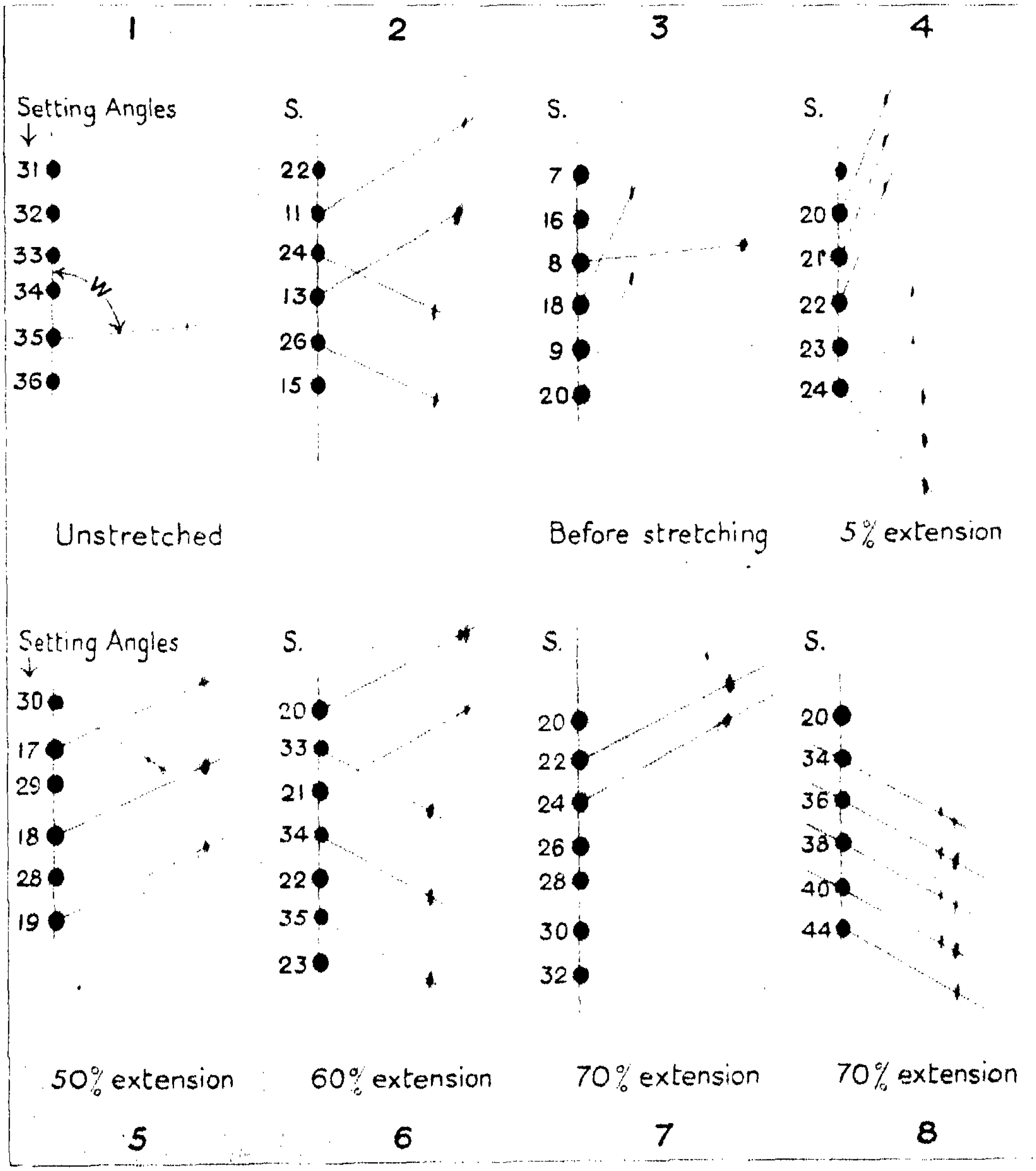
FIG. 3.

We now proceed to calculate θ and ψ from the three measured angles, ϕ, s, w. From the spherical triangle Z, P, P′ in fig. 4 we obtain—

$$\cos\theta = \cos w \,.\, \cos\phi$$
$$\sin\omega = \sin\phi/\sin\theta$$
$$\psi = \omega - s$$

ω is an auxiliary angle which is shown on fig. 4.

These equations enable us to calculate θ and ψ from the three observed angles ϕ, s, w. The problem which is stated at the beginning is therefore solved. A series of these calculated values of θ and ψ is given in Taylor and Elam's paper. (These angles were obtained from measurements on a specimen with square section; the reference plane was one of the boundary surfaces of the specimen.) Their numerical values, as they were obtained from the experiments, have no immediate physical interest. They are not reproduced here for this reason.


Setting Angles
W
S.
S.
S.
Unstretched
Before stretching
5% extension
Setting Angles
S.
S.
S.
50% extension
60% extension
70% extension
70% extension

The X-ray Apparatus.

The X-ray bulb was fitted with a copper anticathode and run by a coil at 40 to 50 kilovolts at something like 5 milliamperes. The exposures varied from 5 to 10 min.

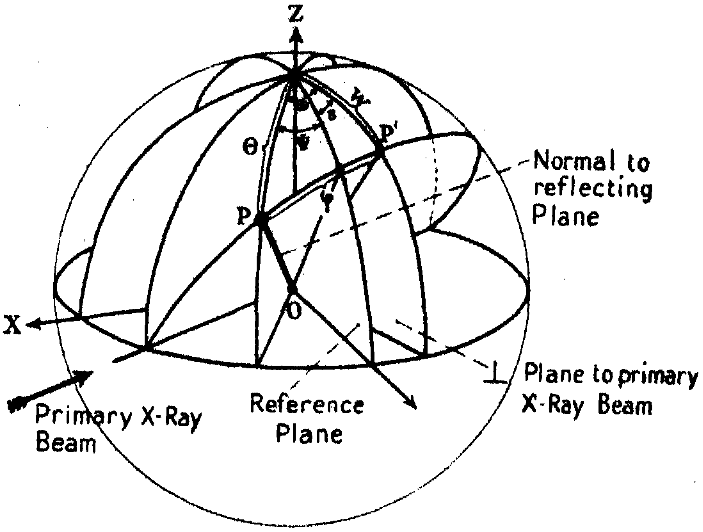


Fig. 4.

Discussion of the Method and the Results.

The method of finding the crystal-axes which has been described in this paper has the disadvantage that the data can only be obtained for a relatively very thin surface layer of the test-piece. Measurements which were made on various parts of the surface showed that this surface layer had the same orientation relative to the reference plane over the whole surface. It was therefore likely that the same thing should hold for the whole bulk of the samples.

It has been pointed out before that the reflection always occurred over a certain range of setting angles. It is of interest to examine the reasons for this effect. One obvious cause is the already mentioned divergence of the primary beam. The influence of this divergence can easily be eliminated. It was found that the reflection range could be explained by the divergence of the primary beam in the case of the unstretched or only slightly extended samples. It was at the same time found that the reflected spots were very small as a rule. As the extension went on, the range of reflection frequently increased, and it was noticed that the size of the reflected spots became larger.

Assuming that the material of the test-pieces breaks up into small crystals as the extension goes on, we can, from the dimensions of the reflected spots, make a rough estimate of the maximum angle between the surfaces of a pair of these small crystals. It was found that this angle amounted sometimes to several degrees. This shows the actual breaking up of the test-piece into smaller crystal aggregates. As these aggregates remain, even after a considerable extension of the test-piece, very nearly in the same average position, the test-piece can microscopically be considered as being a single crystal.

It has been known for some time, and the recent work of Polanyi and his school has emphasised the point, that metals can be brought into a semi-crystalline state by mechanical treatment. Weissenberg* has shown how all the orientation effects can be treated statistically. It seems to the writer that this view of the subject is the most satisfactory at the present stage of development of the subject.

Another point may be mentioned here. A Laue-photograph was taken of a test-piece at the every edge where the sample was broken. The pattern which resulted showed the existence of relatively large crystals very near the edge. This shows that the edge in spite of the violent distortion is by no means in a completely amorphous state.

In conclusion the writer wishes to acknowledge the valuable help which he had from Miss C. F. Elam. The present work was done in the Cavendish Laboratory, Cambridge. The author is very much indebted to Sir Ernest Rutherford for his interest in the work and for the readiness with which he placed the necessary apparatus at his disposal. The writer expresses also his best thanks to Mr. G. I. Taylor who suggested the work.

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* Weissenberg, 'Annalen der Physik,' vol. 69, p. 409 (1922).

Absorption of Hard γ-Rays by Elements.

By N. AHMAD, M.Sc., Peterhouse, Cambridge.

(Communicated by Prof. Sir E. Rutherford, F.R.S. Received March 1, 1924.)

Introduction.

In this paper an account will be given of an accurate determination by a balance method of the relative absorption in a large number of elements of γ-radiation from Ra B + C filtered through 1 cm. of lead. The object of these experiments was to find out whether there is a simple relation between the absorption in an element and its atomic number, and also whether the nuclear electrons make a sensible contribution. As a result of these measurements, it will be shown that the laws of absorption of γ-rays of high frequency can be linked up with the corresponding laws known for X-rays of much lower frequency. A mutual comparison will also throw some light on the relative part played by scattering and true absorption in the passage of penetrating radiation through matter.

An account of earlier work on the absorption of γ-rays by matter will be found in the standard works on radioactivity—*e.g.*, by Rutherford (1913) and by Meyer and Schweidler (1916). It is, however, necessary to mention briefly some results of the later work relevant to the present experiments.

As a result of a thorough investigation, Soddy and Russell* found that γ-rays, after traversing a certain thickness of matter, were absorbed exponentially in all elements. From the values of the mass-absorption coefficient μ/ρ they concluded that elements could be divided into three classes, viz., the heavy ones like Hg or Pb, with μ/ρ large; the intermediate ones like Fe, Cu, Zn, etc., with μ/ρ nearly constant and equal to 0·04; and the light ones, like Al or S, with μ/ρ between those for the first two classes. They showed that in ordinary experimental methods a correction was necessary to take into account the divergence of the primary beam.

Florance† showed that a considerable fraction of the energy of the γ-rays—as much as 30 per cent.—was either scattered or transformed into a secondary radiation, which decreased both in hardness and intensity with the angle made with the incident beam. The necessity of taking this secondary radiation into account was shown by Ishino,[*] who estimated the relative importance of scattering and true absorption for a few elements, and found them of the same order of magnitude. Compton showed that "true" scattering was negligible, the secondary radiation being always softer than the primary.

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* 'Phil. Mag.,' vol. 18, p. 620 (1909); vol. 19, p. 725 (1910); vol. 21, p. 130 (1911).

† 'Phil. Mag.,' vol. 20, p. 921 (1910).

It is now well known that the γ-rays from RaB + C are very complex in character. This has been shown directly by Rutherford and Andrade's[†] examination of the rays by the crystal method, and confirmed indirectly by the absorption experiments of Rutherford and Richardson[‡] and those of Kohlrausch.[§] From a study of the magnetic spectrum of β-rays from RaB + C, it is clear that γ-rays are emitted over a wide range extending to wave-lengths as short as 0·005 Å.U. By a development of this method the wave-lengths of some of the hard rays from RaB + C have recently been measured by Ellis[||] and Ellis and Skinner.[¶]

General Considerations.

In a usual absorption experiment on such a complex beam the quantity actually measured is the *averaged* coefficient for a mean effective wave-length. This quantity always contains a term depending upon the amount of secondary radiation entering the ionisation chamber. Both this term,[**] and the mean effective wave-length are complicated functions of the total thickness; and our theoretical knowledge is not adequate to enable us to correct for different ranges of thickness.

Now in previous experiments the total thicknesses of the various absorbers used have more or less been determined by the availability of the material. It is clear that in this way strictly comparable results would not be obtained.

For an accurate comparison it is desirable to adopt the plan of having all the absorbers of the same linear dimensions, and with thicknesses so adjusted that the absorption in each substance is about the same. Since the secondary radiation produced is proportional to the primary absorbed, the correction due to scattering will be the same for all elements. The mean effective wave-length will also be constant throughout.

Thick lead slits, described later, served not only to give a uniform size to the absorbers but also to admit only a definite fraction of the secondary radiation into the ionisation chambers. These latter were so constructed as to absorb practically all the rays entering them. The accuracy was considerably increased by using a balance method with Al as the standard absorption substance.

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[*] 'Phil. Mag.,' vol. 33, p. 140 (1917).

[†] 'Phil. Mag.,' vol. 27, p. 854 (1914); vol. 28, p. 263 (1914).

[‡] 'Proc. Roy. Soc.,' A, vol. 91, p. 396 (1915).

[§] 'Wiener Berichte,' vol. 126, p. 441 (1917).

[||] 'Proc. Roy. Soc.,' A, vol. 99, p. 261 (1921); vol. 101, p. 1 (1922).

[¶] 'Proc. Roy. Soc.,' A, vol. 105, p. 165 (1924).

[**] See Ishino, *loc. cit.*

Apparatus and Method.

The Absorbers.—Except in the case of H and O, the elements or their oxides were used as absorbers. The thicknesses were such as to produce an absorption of 15 to 18 per cent. The elements, in the form of plates, were :—

C, S, Fe, Ni, Cu, Zn, Ag, Sn, Pt, Pb, and Bi.

Of these C and Bi were 11 cms. sq., S and Ag 16 cm. sq., Pt 5 cm. sq., and the rest 20 cm. sq. The oxides, ThO_2 and U_3O_8, and also Hg, were contained in rectangular glass cells 16 cm. sq. The correction due to the glass was found by repeating the experiment with an extra glass plate of known thickness on each side of the cell. With Th and U the effect of the weak γ-radiation given out was allowed for by measuring it in the absence of the sources. The value for H was deduced from measurements on paraffin wax, and that for O from water.

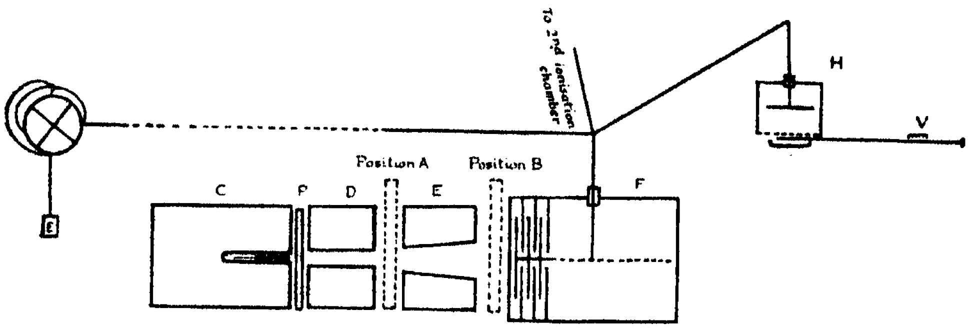

Fig. 1. The Apparatus

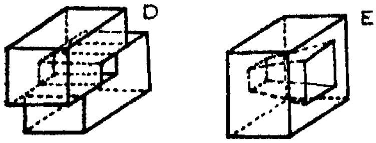

Fig. 2. The Slits

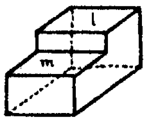

Fig. 2a

Apparatus.—The apparatus used is shown in fig. 1. As the two sides are similar, it will be sufficient to describe only one. The source (about 7 mgs. $RaBr_2$) was put inside a narrow circular hole in the middle of the lead cylinder C. Immediately in front of it was a lead plate P, 1 cm. thick ; and next to it the adjustable slit D. This is shown in greater detail in fig. 2, and was made by placing together two lead blocks, each of the shape shown in fig. 2A. The plane surface *m* being 2·5 cms. lower than *l*, when the blocks were in position the upper one could be moved by a screw, and a rectangular slit of variable width obtained. The motion of the screw was calibrated in terms of deflections per minute. The width of the corresponding slit on the other side was kept constant at 2·50 cms. This arrangement gave a very well-defined beam. The second "slit" E, in the middle of a block of lead, was in the form of the frustum of a pyramid, of such dimensions as just to allow the divergent primary beam to pass through. This is also shown in fig. 2.

The ionisation chamber F, supported on paraffin blocks, was a rectangular box of sheet lead 0·16 cm. thick, and divided inside by iron plates into a number of compartments, each with a circular iron plate as its electrode. These plates were carried by a central horizontal rod supported by a vertical rod passing through the ebonite plug. The interior of the chamber was lined with thin aluminium foil. This model is due to A. H. Compton. A large stone block and lead screens between the two chambers prevented cross-scattering. On one side a movable clamp held the absorbers in position.

A Bronson uranium oxide resistance, H, was used to balance the small natural leak of the apparatus. It consisted of a cylindrical ionization chamber with a base of wire gauze, resting over some U_3O_8 in a shallow dish. A Zn plate, attached to a vernier V, could uncover as much of the dish as required.

The electrode wires, all carefully shielded, were connected as shown to the electrometer, which was of the Compton type. With 50 volts on the needle, it gave a sensitivity of about 5,000 mms. per volt. The positions of the slits D and E with respect to the source and the chamber were adjusted by substituting a pea lamp for the source.

Method.—The two ionization chambers were charged to ± 80 volts and the resistance H to + 120 volts. Without the sources, the natural leak was balanced against H to within 2 div./min. With the sources, the slit D was adjusted until the difference between the two ionization currents (each of the order of 1,300 div./min.) was between 1 and 3 div./min. This deflection was carefully timed. Now the absorber, as well as the aluminium, could be placed either near the source (denoted as position A) or near the ionization chamber (B). Consequently, the following four variations were possible :—

$\left.\begin{array}{l}\text{Absorber at A}\\ \text{Aluminium at A}\end{array}\right\}$ Position I.

$\left.\begin{array}{l}\text{Absorber at B}\\ \text{Aluminium at B}\end{array}\right\}$ Position II.

$\left.\begin{array}{l}\text{Absorber at B}\\ \text{Aluminium at A}\end{array}\right\}$ Position III.

$\left.\begin{array}{l}\text{Absorber at A}\\ \text{Aluminium at B}\end{array}\right\}$ Position IV.

As the method for dealing with the four positions differed but little, position I alone will be considered in detail. The absorber being held vertically between D and E, aluminium plates were put between the slits on the other side. Corresponding to different total thicknesses of aluminium, two deflections, one a little on each side of the null point, and for position I a third very close to it, were carefully timed. From these, after correcting for the small balance 'leak,' the exact thickness of aluminium producing the same absorption as the absorber was found by interpolation. Finally, aluminium in position A was balanced against itself in position B.

Actually, instead of thickness, mass per unit area is employed in calculations, so that the uncertain knowledge of densities is not involved. The ratio of the masses per unit area that balance each other is equal to the inverse ratio of the apparent mass-absorption coefficients :

$$\frac{\mu_1}{\rho_1} : \frac{\mu_2}{\rho_2} = \frac{\rho_2 l_2}{\rho_1 l_1}.$$

The mass-absorption coefficients for aluminium itself in positions A and B were determined directly. That for position B could also be calculated from that of A, and the ratio for Al in the two positions found previously. The two results agreed to within ½ per cent.

Each reading was repeated about ten times, the experiments for position I at least twice, and the determination of coefficients for Al several times. All readings were referred to a fixed sensitivity of 5,000 div./volt. This was actually found to fluctuate between 4,500 and 5,000.

A Typical Experiment and Probable Error.

For purposes of illustration, the measurements relating to copper in position I are reproduced. Mass per unit area of Cu plate = 4·596 gms./sq. cm.

Position I.—

Mass per unit area of Al plates.	Mean corrected deflection (div./min.).	Equivalent mass per unit area of Al.
(*a*) Natural leak = − 1·5 divisions/minute.		
4·190 gms./sq. cm.	− 13·9	4·485 gms./sq. cm.
4·484 ,, ...	+ 0·6	
4·777 ,, ...	+ 13·3	
(*b*) Natural leak = − 3·9 divisions/minute.		
4·333 gms./sq. cm.	− 7·6	4·491 gms./cm.
4·769 ,, ...	+ 12·2	

The readings in the second column could be measured to 1 div./min. ordinarily, and to 0·5 div./min. by repeating the experiment. Now a deflection of 1 div./min. was produced by 0·008 cms. of Al, and as the average thickness of Al used was 1·65 cms., the error involved was 1/200 in a single experiment and 1/400, or less, if repeated.

The errors due to slight temperature and pressure variations, and those involved in the determination of masses per unit area, were comparatively negligible. A small error of uncertain magnitude, affecting the positions IV, III, II in increasing order, arose through the difficulty of so adjusting the positions of the absorbers and aluminium plates as to admit *exactly* the same amount of secondary radiation into the ionization chambers.

Results.

The experimental results are given in Table I. The discussion of columns II-IV is postponed to a subsequent paper, and the results in column I, which are the mean of the experimentally determined values shown under I′, alone will be considered here.

These represent the ratios $\left(\frac{\mu}{\rho}\right)_{\text{Al}} \Big/ \left(\frac{\mu}{\rho}\right) = \text{P}$ (say) when the secondary rays are, as far as possible, excluded from the ionization chamber. A comparison with previous work is only possible in cases where conditions were, roughly, similar, as in some of the experiments of Soddy and Russell. Calculating P from their results, we find :—

	S.	Fe.	Cu.	Zn.	Sn.	Hg.	Pb.
S. and R.	0·915	1·005	1·008	1·020	1·034	0·848	0·922
A.	0·950	1·017	1·024	1·026	1·011	0·813	0·838

which shows a general agreement.

Comparison with later work is not possible, as in almost all cases the absorption curves were analysed to find the coefficients of the main constituent groups of the beam, *e.g.*, Kohlrausch.*

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* *Loc. cit.*

Table I.

Element.	I′.	I.	II.	III.	IV.
H	0·490 0·486	0·488	—	—	—
C	0·959 0·956	0·958	0·882	1·039	0·792
O	0·965	0·965	—	—	—
Al	1·000	1·000	1·000	1·183	0·845
S	0·942 0·959	0·950	0·909	1·074	0·777
Fe	1·015 1·019	1·017	0·989	1·201	0·856
Ni	0·991 0·995	0·993	0·968	1·138	0·835
Cu	1·022 1·024 1·024	1·024	1·003 1·014	1·216 1·209	0·861 0·860
Zn	1·024 1·028 1·027	1·026	0·981	1·161	0·852 0·848
Ag	1·010 1·013	1·012	0·998	—	0·855
Sn	1·012 1·012 1·008	1·011	0·953	1·146	0·846
Pt	0·838 0·840	0·839	—	—	—
Hg	0·812 0·814	0·813	—	0·916	—
Pb	0·838 0·837	0·838	0·772	0·917	0·705
Bi	0·807 0·810	0·809	—	—	—
Th	0·705	0·705	—	—	—
U	0·691	0·691	—	0·761	0·542

$\left(\frac{\mu}{\rho}\right)_{Al}$ in position A = 0·0490 ; in position B = 0·0416.

Discussion.

An examination of column I shows that it is not possible to represent the absorption results by any such simple scheme as that suggested by Soddy and Russell or Kohlrausch. If the absorption of the rays were simply proportional to the mass traversed by them, the ratios (P) should be equal to unity in all cases. Actually not only is the deviation from unity in each case outside the experimental error, but the values vary irregularly among themselves, and the variation seems to bear no relation to atomic weight or atomic number. To find the physical significance of the results some more fundamental quantity, such as the absorption per atom, or as is slightly more convenient, the absorption per electron[*] must be considered.

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[*] We are referring here to extra-nuclear electrons.

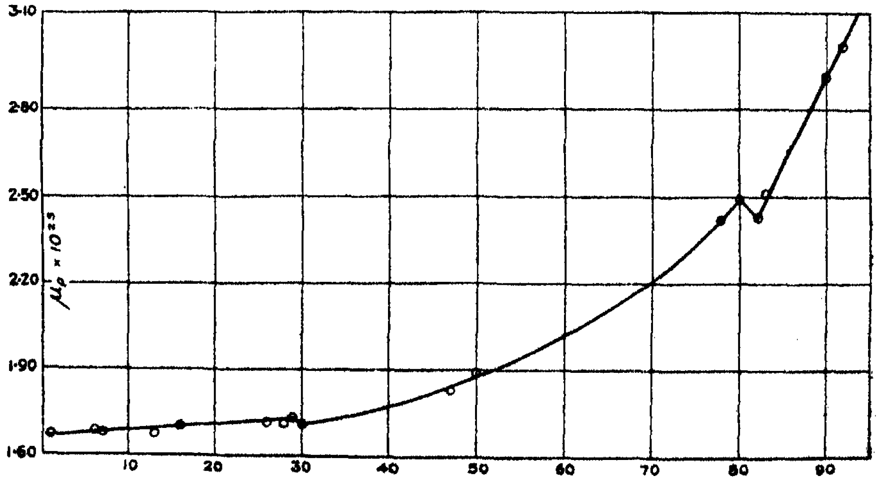
This latter quantity, denoted by μ_e, is readily seen to be given by

$$\mu_e = \frac{\mu}{\rho} \cdot \frac{1}{N} \cdot \frac{A}{Z} = \frac{\left(\frac{\mu}{\rho}\right)_{Al}}{P} \cdot \frac{1}{N} \cdot \frac{A}{Z},$$

where N is Avogadro's number, A the atomic weight and Z the atomic number of the element. The calculated values for μ_e are given in Table II, where N is taken equal to $6 \cdot 06 \times 10^{23}$ and $(\mu/\rho)_{Al} = 0 \cdot 0490$. These values are plotted against Z in Graph I. It will be seen that, except for a discontinuity between Hg and Pb, discussed later, the curve is smooth and anomalous

Table II.

Element.	Atomic Number.	Absorption per electron $\times 10^{25}$.
H	1	1·668
C	6	1·688
O	8	1·675
Al	13	1·676
S	16	1·706
Fe	26	1·709
Ni	28	1·706
Cu	29	1·731
Zn	30	1·718
Ag	47	1·833
Sn	50	1·897
Pt	78	2·420
Hg	80	2·494
Pb	82	2·437
Bi	83	2·516
Th	90	2·917
U	92	3·028



GRAPH I.

fluctuations do not appear. Before attempting to discover the general physical significance of the curve, it is desirable to mention three particular points in connection with it.

(*a*) *Case of Hydrogen.*—Hydrogen was one of the last-tried elements. It was concluded from the linear part of the curve that its mass-absorption coefficient should be nearly twice as great as for any of the light elements, so that P would be slightly less than one-half. Actually it was found to be 0·494. This at once explains the abnormally large absorption, observed by all previous workers, in such substances as paraffin, wood, water, etc. It also throws some light on the process of absorption, for it shows that the protons in hydrogen, though as numerous as the electrons, do not play any appreciable part in the absorption or scattering of hard γ-rays.

(*b*) *Drop after Hg.*—A certain amount of *k*-radiation of lead will be present in the primary beam. Part of it will be excited, as shown by Gray, in the lead plate by the hard γ-rays, and part will be emitted, as shown by Rutherford and Andrade, by Ra B (isotopic with Pb). We should, therefore, expect lead to be exceptionally transparent to the beam and, consequently, a sudden fall in absorption just before it. To test this explanation Sir E. Rutherford suggested placing a small thickness of lead sheet before each ionization chamber. The absorption coefficient of K-radiation of lead, according to Rutherford, being 22 (cm.)$^{-1}$, just below the K-absorption band, 3 mm. of Pb should practically eliminate the discontinuity. The results of such experiments were :—

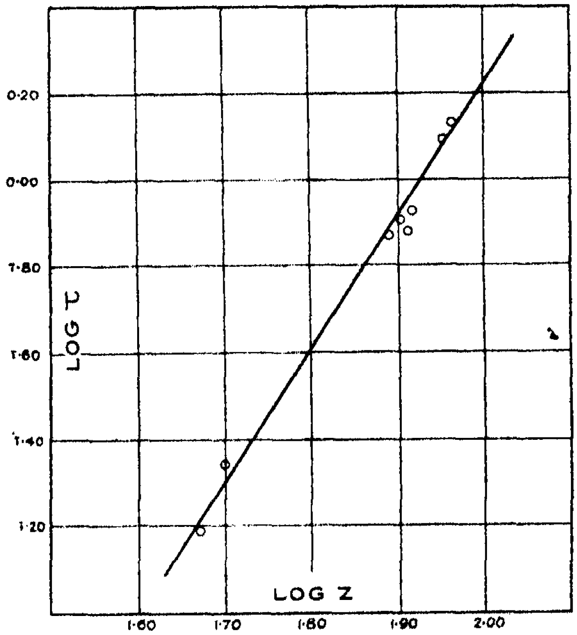
Thickness of Pb (mm.)	μ_e
0·0	$2{\cdot}494 \times 10^{-25}$
1·0	2·466
3·0	2·424

which support the explanation offered. That the "kink" is much smaller and less sharp than those occurring in X-ray absorption phenomena is presumably due to the relatively small proportion of the characteristic radiation present.

(*c*) *Drop after Copper.*—It will be noticed that there is also a small "kink" between Cu and Zn. This has appeared consistently in repeated experiments, and, though it is quite within the experimental error, it may be due to the excited L-radiation from lead. The longest wave-length in this (1·34 Å.U.) is smaller than the κ-absorption limit of Cu (1·38) but greater than that of Zn (1·29).

General Absorption Formula.

We must now consider the general features of the absorption curve. It will be noticed that the absorption per electron increases very slowly at first with the atomic number, but rapidly after 40. If the value for Al be subtracted from the ordinates of the curve, and the differences plotted logarithmically



GRAPH 2.

against Z, we obtain Graph II. The slope is almost exactly 3, and it gives for the equation to the main curve I,

$$\begin{aligned} \mu_e &= 1 \cdot 68 \times 10^{-25} + 1 \cdot 60 \times 10^{-31} Z^3 \\ \text{or}\ \mu_A &= 1 \cdot 68 \times 10^{-25} Z + 1 \cdot 60 \times 10^{-31} Z^4 \qquad (1) \\ &= a Z + b Z^4, \end{aligned}$$

where μ_A is the *absorption per atom.* The close analogy of this formula to

$$\mu_A = \alpha Z + \beta \lambda^3 Z^4,$$

which by general agreement best represents X-ray absorption results, is evident, and suggests that the two processes are not fundamentally different. We may, therefore, consider the first term to represent the part of apparent absorption due to scattering, and the second term a kind of " true " absorption such as is connected with photo-electric emission. The relative importance of the two terms is best shown by a numerical example. Denoting the first term of the formula by σ, and the second by τ, (1) may be written as

$$\mu_A = \sigma + \tau.$$

The ratios of the scattering to the true absorption for Al and Pb, typical light and heavy elements, are given in the following table for $\lambda = 0 \cdot 02$ Å.U., the values for $\lambda = 0 \cdot 2$ Å.U. being added for comparison.

λ	0·02	0·2	
Al	427·0	1·24	σ/τ.
Pb	1·7	0·005	

The figures show that for 0·02 Å.U. the true absorption, while negligible for Al, is comparable with the scattering for Pb. We should therefore expect the photo-electrons constituting the ordinary β-ray magnetic spectra, to be given out with measurable intensities only by the heavy elements. This is in agreement with Ellis' observations on hard γ-rays.

We will now consider each term separately.

The Scattering Term.—It will be noticed that for low atomic weight elements practically the whole of the absorption, and in high atomic weight ones at least one-half of it, is due to scattering alone. According to J. J. Thomson's classical theory the term representing it should be given by $\sigma_0 Z$, where

$$\sigma_0 = \frac{8\pi}{3} \frac{e^4}{m^2 C^4} = 6 \cdot 64 \times 10^{-25}.$$

But even for moderately hard X-rays the value satisfying the experimental results is of the order of $0 \cdot 8\ \sigma_0 Z$,* and for these extremely short wave-lengths we should expect it to be still smaller.† In an extension of his quantum-classical treatment of scattering, Compton‡ has deduced for the total scattering absorption the formula

$$\sigma = \frac{1}{1 + 2\alpha} \sigma_0, \quad \text{where} \quad \alpha = \frac{0 \cdot 0242}{\lambda \text{ (in Å.U.)}}.$$

If this result be utilised, the effective wave-length of the rays employed may be approximately estimated. It leads to the value $\lambda = 0 \cdot 015$ Å.U. A fuller discussion of this term, however, would involve considerations of Columns II–IV, and is reserved for a subsequent paper.

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* Hewlett, 'Phys. Rev.,' vol. 17, p. 284 (1921); Richtmeyer, 'Phys. Rev.,' vol. 18, p. 13 (1921).

† See pp. 37 and 32, 'Bull. Nat. Res. Council,' vol. 20 (1922).

‡ 'Phys. Rev.,' vol. 21, p. 207 (1923).

The Absorption Term.

Applying quantum considerations to photo-electric interaction between radiation and atoms, de Broglie and more recently Kramers* have derived the formula

$$\tau_A = \beta' \lambda^3 Z^4,$$

which is known to represent X-ray absorption results. The energy absorbed is assumed to be spent in removing electrons from the various levels, and since exactly similar considerations would apply for γ-rays, the second term undoubtedly represents a kind of true absorption.

It seems unlikely that the constant b for the γ-ray absorption term will have a value different from what is found from X-ray measurements. Taking Richtmeyer's latest value for β ($2 \cdot 24 \times 10^{-2}$), we obtain

$$2 \cdot 24 \times 10^{-2} \lambda^3 = 1 \cdot 60 \times 10^{-31}$$

or

$$\lambda = 0 \cdot 019 \text{ (Å.U.)}.$$

This result agrees with what would be anticipated from general considerations of β-ray spectra combined with Ellis's measurements. The evidence for the λ^3 law for *homogeneous* X-rays for radiation of wave-lengths much shorter than the K is very strong,† and there can be little doubt as to the justification of this tentative extrapolation to γ-rays. But it must be remarked that the above value represents the cube-root of $\frac{\Sigma I_\lambda \lambda^3 \delta\lambda}{\Sigma I_\lambda \delta\lambda}$ instead of the mean wave-length, and will consequently give a larger estimate than the arithmetic mean. Moreover, the absorption increasing as the cube of the wave-length, the very hard rays, whose presence is strongly suggested by indirect evidence, may escape detection. Experiments in this direction, however, are in progress.‡

Further, in the X-ray region for $\lambda < \lambda_k$ the absorption corresponding to the K, L, M . . . levels decreases fairly rapidly. The ratio of K to L absorption is of the order 6, and the theoretical indications§ are that these ratios are independent of wave-length. We should, therefore, expect γ-rays to be absorbed strongly in the innermost levels. This is borne out by Ellis's observation that the strongest lines in his spectra were from the K-level, and the next strongest from the L-levels.

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* 'Phil. Mag.,' vol. 46, p. 275 (1923).

† Richtmeyer and Warburton, 'Phys. Rev.,' vol. 22, p. 539 (1923).

‡ It should be noted that no *proof* of the validity of λ^3 law for these high frequencies is here advanced. The relation discovered shows simply that the apparent atomic absorption of hard γ-rays is proportional to Z^4. The second term would probably be of the general form $\beta f(\lambda) Z^4$, where the determination of $f(\lambda)$ would involve further data as to the intensities and wave-lengths of the high-frequency γ-rays.

§ Kramers, *loc. cit.*

It is noteworthy that within the accuracy of these experiments, no effects due to nuclear absorption have been discovered. The absorption of the hard γ-rays, which most probably have their origin within the nucleus, appears to follow the same general law which holds good for X-rays, which undoubtedly originate in the extra-nuclear structure.

Summary.

By means of a balance method the absorption of hard γ-rays from Ra B + C has been measured with considerably greater accuracy than hitherto, and for a larger number of elements.

The results indicate that the relations governing the apparent absorption are of the same type as for X-rays. The apparent atomic absorption can be represented by

$$\mu_A = 1 \cdot 68 \times 10^{-25} Z + 1 \cdot 60 \times 10^{-31} Z^4.$$

Taking the first term to represent scattering absorption, and the second photo-electric absorption, two estimates of the mean effective wave-length have been obtained (0·015 and 0·019 Å.U.), which are in fair agreement between themselves and with the indications of other work.

Acknowledgments.

My best thanks are due to Prof. Sir Ernest Rutherford for his kind and stimulating interest, and to my friend E. C. Stoner for his constant and invaluable help.

On Selective Absorption by Luminous Mercury Vapour.

By E. P. Metcalfe and B. Venkatesachar.

(Communicated by Prof. A. W. Porter, F.R.S.—Received January 1, 1924.)

[Plate 5.]

In a previous paper published by the authors* there were described, among others, experiments on the reversal of the main component of the 5461 A group of lines and its brightest satellite + 0·085 A in the spectrum of the low-pressure mercury vapour lamp. McLennan, Ainslie and Miss Cale† have repeated these experiments and, in the main, confirm the results obtained by us. They, however, point out that what is taken as the main component when the green radiation is examined in instruments of resolving power of the order of 200,000 is a group of five lines of wave-lengths − 0·020 A, − 0·008 A, 0, + 0·008 A, and + 0·018 A ; and they state that only the three central lines are absorbed by luminous mercury vapour, the unabsorbed satellites + 0·018 A and − 0·020 A producing the appearance of reversal. They also describe experiments which, they consider, indicate the absence of absorption in the case of all the other components of this group, including + 0·085 A. This last result is at variance with our observation of the reversal of this satellite, recorded in the paper cited above.

To clear up this point we undertook a systematic investigation of the absorption of the satellites of the three lines 5461 A, 4358 A, and 4047 A ($1p_1 - 1s$, $1p_2 - 1s$, and $1p_3 - 1s$ on Fowler's notation) the first triplet of the second subordinate series of triplets. We have observed marked absorption, under suitable conditions, in the case of all the satellites of the group 5461 A, excepting one, viz., − 0·237 A, and have reversed five of them. We find that even − 0·237 A shows feeble, but distinctly perceptible, absorption under exceptionally favourable conditions. In the present paper we describe the behaviour of the luminous vapour in regard to the members of this group (5461 A, $1p_1 - 1s$).

We have previously pointed out certain facts indicating the existence of absorption in the case of some of the satellites ; for example, (1) it was noticed that the brightness of the satellites tended to equalise as the length of the radiating column increased; and (2) the unabsorbed fraction of the light from a radiator, probably representing the satellite radiation, was found to be diminished by increasing the length of the absorbing column without changing the current density in it. From a consideration of the latter fact, it is possible to make a rough estimate of the coefficient of absorption of the satellites, as a group, apart from the main line.

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* 'Roy. Soc. Proc.,' A, vol. 100, pp. 149–166 (1921).

† 'Roy. Soc. Proc.,' A, vol. 102, p. 33 (1922).

For if R is the radiation of this group from the source and A is the coefficient of absorption per unit thickness of the absorbing vapour for the group, then R_t the light transmitted by an absorbing column of length x is given by

$$R_t = Re^{-Ax}.$$

Similarly for an absorbing column of length x'

$$R_t' = Re^{-Ax'}.$$

From these we have

$$R_t/R_t' = e^{-A(x-x')}.$$

Taking values from our paper under reference (p. 154), we have $R_t/R_{t'} = 0{\cdot}33/0{\cdot}22$, and $x' - x = 35 - 13 = 22$ cms. for a current density in the absorbing column of about 13·4 milliamps./sq. cm. This gives for A the value 0·018. For the same current density the absorption coefficient, as calculated from data on p. 156, for the heavily absorbed main line is 0·26. (This "main line" is in reality a close group of lines, as has been pointed out.) This indicates that the average absorption of the satellites is so small compared with the absorption of the main line that strong absorption of satellites will only be visible under specially favourable conditions; and the conditions must be still more carefully adjusted in order to produce definite satellite reversals.

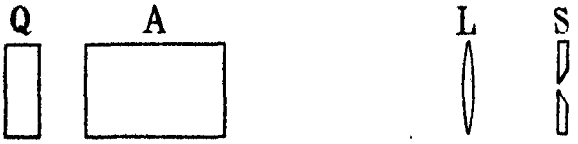

FIG. 1.

In fig. 1 Q represents a radiator, the light from which passes through an absorbing column A to a converging lens L and thence to S, the slit of the observing spectroscope. Let Q and A be close together and sufficiently far from L, so that the images of all parts of both Q and A may be considered sharply focused on the slit together. Let R be the intensity of radiation of the source Q. After absorption in A the intensity will be Re^{-Ax}, where A is the absorption coefficient and x is the length of the absorbing column. The intensity of radiation of the absorber is $(E_a/A)(1 - e^{-Ax})$, where $E_a \, . \, dx$ is the intensity of radiation of a thickness dx of the absorbing column. The illumination on the slit is proportional to I, where

$$I = Re^{-Ax} + (E_a/A)(1 - e^{-Ax}).$$

Hence when the absorber current is switched on, the loss of illumination on the slit is proportional to $R - I$, where

$$R - I = (R - E_a/A)(1 - e^{-Ax}).$$

If $R - I$ is positive, *i.e.*, if $R > E_a/A$, it will be theoretically possible to observe a diminution of brightness at S when the absorbing column current is switched on.

We have previously shown (*loc. cit.*) that, for small current densities, E_a/A is proportional to i, the current density in the absorbing column; so that the condition for diminution of brightness reduces to $R > ki$, where k is a constant.

This condition may be fulfilled for any value of R, however small, by sufficiently reducing i. But a reduction in i leads to a corresponding reduction in A, which increases the term $(1 - e^{-Ax})$ in equation (1), and thus reduces $R - I$. To compensate for this it will be necessary to increase x. The change of brightness is most marked when e^{-Ax} is negligible in comparison with unity, *i.e.*, when Ax is large. In this case $I = E_a/A$, and the effect of introducing the absorbing column is to cut out the illumination due to Q and to substitute that due to the absorbing column itself. Thus, by sufficiently reducing the current in the absorbing column and correspondingly increasing its length, it must always be possible to reduce the illumination at S to any desired extent. Under these conditions, if Q produces a continuous spectrum, there will be a local diminution of brightness resulting in a reversal, provided the resolving power of the observing instrument is sufficiently great.

These considerations led us to construct an absorption apparatus permitting of the use of longer columns than those we had previously employed. As before, the necessary ionisation was produced by a subsidiary arc in a side tube joined to the middle of the main absorption tube (*see* fig. 2).

The absorption tube was provided with two hollow cylindrical anodes of iron: the anodes were connected to steel caps in which fitted the quartz lenses closing the ends of the tube. The apparatus was exhausted through side tubes let into the steel caps. It was found necessary to exhaust from both ends of the apparatus in order to prevent an accumulation of diffused gas at the closed end. The length of the tube between the electrodes was lagged with asbestos and was kept hot during an experiment by means of an electric heating coil (not shown in the diagram) wound non-inductively to obviate any possible magnetic effect on the absorption lines. The internal diameter of the absorption tube was 3·5 cms., and the distance between the iron anodes was one metre. In order to maintain steady arcs between the common kathode, K, and the two iron anodes simultaneously, each anode was fed from a separate battery system, the available voltage on each anode being 280. The currents in the two circuits were regulated by suitable rheostats. The necessary high vacuum was maintained by liquid air-cooled charcoal.

Our first experiments were directed to testing an observation recorded in our previous paper of the absorption of the satellite + 0·085 A, which McLennan and his collaborators failed to verify. Using a low-pressure mercury arc as radiator and a Lummer-Gehrcke plate of resolving power about 200,000 at 5461 A, we isolated the satellite + 0·085 A by means of a shutter eye-piece, so that no other constituents of the group were visible. On switching a current of density 10 milliamps./sq. cm. in the whole length of the absorbing column, *i.e.*, one meter, we found that the satellite was nearly extinguished.

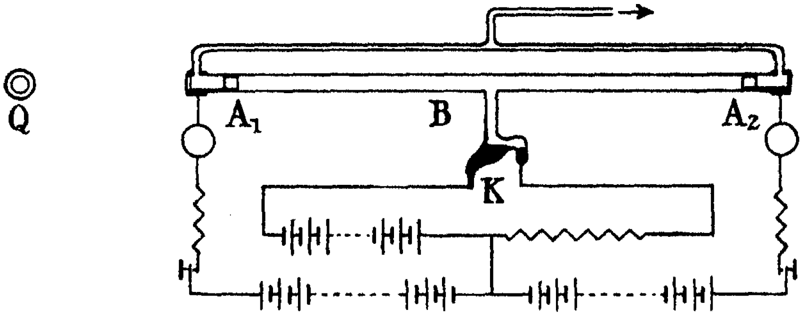

FIG. 2.

Other satellites treated in the same way also showed considerable absorption —an important exception, to which further reference will be made, being the satellite − 0·237 A, the absorption of which was only just perceptible under the most favourable circumstances.

We next attempted to produce reversals of as many satellites as possible. For this it was necessary to employ an intense source, giving lines so widened as to furnish a small portion of continuous spectrum of sufficient extent to form a background. A suitable source was found in the form of an "end-on" silica lamp made by the Hewittic Co. With this lamp, carrying one ampere, the mercury vapour pressure rises sufficiently to produce the necessary broadening of the lines. With this arrangement, using the double column of one meter in length, carrying a current of density 10 milliamps./sq. cm., switching on the absorbing current caused a system of dark bands to appear across the widened spectra seen with the Lummer-Gehrcke plate. The main component, already faintly self-reversed in the light from the radiator lamp, became much darker. Including the reversed main component, five dark bands crossed each order of the spectra; one of these was evidently a close double. The effect is well shown in the photograph (Plate 5, fig. 1). In this the absorption spectrum marked *a* is contrasted against the widened line "background" spectrum marked *b*, given by the high-pressure lamp.

The pointer of the eye-piece of the observing telescope was adjusted in succession to each of the following satellites in the bright-line radiation given out by the column alone (supplied with a heavier current for the purpose), viz., + 0·085 A, + 0·128 A, − 0·102 A, and − 0·070 A, and a dark line of the absorption spectrum was found to coincide in each case. The coincidences are shown in the photograph (Plate 5, fig. 2), where the absorption spectrum marked *a* is compared with the emission spectrum marked *b* furnished by the end-on radiation from the long column at very low pressure. It will be seen that each emission line, with the exception of − 0·237 A, corresponds to an absorption line. In the case of − 0·070 A the reversal line appeared double. A diagram of the line system given by our Lummer-Gehrcke plate is shown in fig. 3. The full lines represent satellites in the *n*th order, while the dotted lines represent those belonging to the $(n + 1)$th order. From this it will be seen that near + 0·214 A of the *n*th order, there will be two other lines − 0·070 A and − 0·047 A of the $(n + 1)$th order. The lines + 0·214 A and − 0·070 A are too close for separation: the reversal double line we observe in this region consists probably of + 0·214 A and − 0·070 A reversed together and − 0·047 A. This group of three lines is marked F in fig. 3, and also in the bright line spectrum shown in Plate 5, fig. 3. If consecutive orders of spectra had not overlapped the absorption lines would have been still more marked, since, in that case, a neighbouring widened line of a different order would produce no illumination in the region of reversal of the satellite.

It is of interest to recall an observation reported by Janicki[*] of the appearance in the spectrum of the light from a small Heræus lamp of five equidistant bands replacing the usual 5461 A group. Prince Galitzin and

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[*] Janicki, 'Ann. der Phys.,' vol. 19, p. 35 (1906).

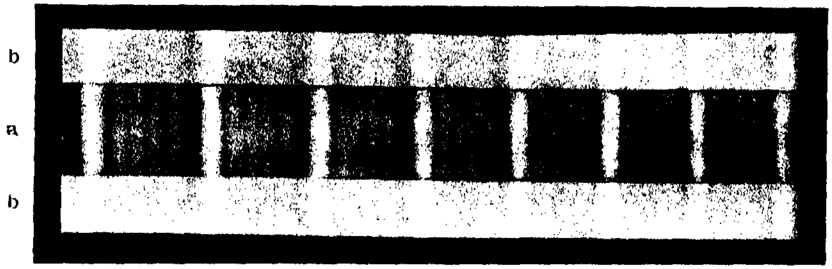

Fig. 1.

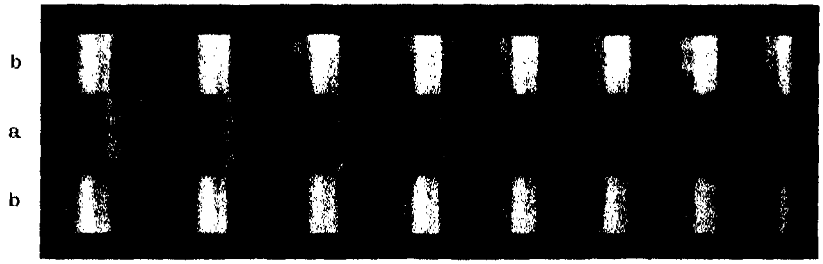

Fig. 2.

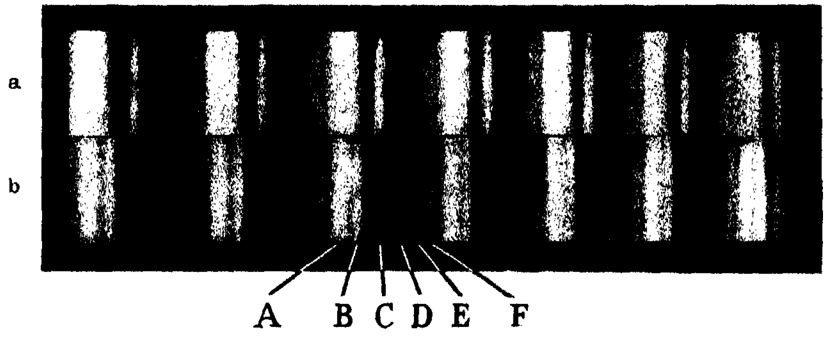

Fig. 3.

Wilip* suggest that this appearance may have been produced by the reversal of the satellites or by some property of the resolving apparatus.

Stanfield† attributes the bands to the secondary spectra of the echelon grating used. McLennan,‡ on the other hand, puts forward the view that the effect may have been caused by the reversal of the main component, accompanied by a strengthening of the satellites. The resemblance between Janicki's rough drawing of the appearance, and the reversal pattern now obtained by us, if we make allowance for the transient nature of the bands seen by him, which must have made the accurate recording of their relative positions a matter of great difficulty, suggests that what he saw was an actual self-reversal of the satellites during the short period for which conditions of pressure and temperature in his lamp were favourable.

According to Nagaoka§ the unresolved group constituting the main line given by our apparatus consists of five components of wave-lengths

$$-0\cdot020\text{ A},\ -0\cdot008\text{ A},\ 0,\ +0\cdot008\text{ A},\ +0\cdot018\text{ A}.$$

McLennan and his collaborators consider that the reversal observed by them is due to the absorption of the three central lines, and state that the outer lines ($-0\cdot020$ A and $+0\cdot018$ A) are unabsorbed. We have tested this conclusion by passing a small current of the order of 1 milliamp./sq. cm. in the column A_1B (fig. 2). This causes an apparent reversal in the main line from a low-pressure radiator placed at Q, leaving the outer components, $-0\cdot020$ A and $+0\cdot018$ A brighter than the central portion of the composite line. A current of the order of 10 milliamps./sq. cm. was then turned on in the column BA_2; the effect of this was to obliterate the two side components. Under these conditions the neighbouring line in the Lummer-Gehrcke plate spectrum, $-0\cdot237$ A, stood out very bright and sharp. We repeated the observation with a small echelon of resolving power 100,000, in the spectrum of which the component $-0\cdot237$ A is not in the close vicinity of the main line group. With the echelon the small current in the first column produced a fine reversal line in the middle of the main line group; the larger current in the second column cut out what was left of the previously unabsorbed wings of the line. The experiment with the echelon was even more striking than with the plate, because of the absence of the complication caused by the enhancement, in the latter case of $-0\cdot237$ A.

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* Galitzin and Wilip, 'Bull. de l'Acad. Sc. de St. Pétersbourg,' 1907, p. 159.

† Stanfield, 'Phil. Mag.,' Sept. (1909), vol. 18, p. 395.

‡ McLennan, 'Roy. Soc. Proc.,' A, vol. 87, p. 273 (1912).

§ Nagaoka, 'Proc. Tokyo Math. Soc.,' 2nd Ser., vol. 8, No. 8, p. 229 (Oct., 1915).

The heavy absorption of all the satellites, except $-0 \cdot 237$ A, may be very clearly demonstrated by the following experiment. The apparatus is arranged as in fig. 2, the radiator Q being, however, absent and the observing spectroscope being a considerable distance from the column. On passing a comparatively heavy current of about 100 milliamps./sq. cm. in the column A_1B, the interference pattern of the Lummer-Gehrcke plate shows the satellites greatly enhanced in brightness. If now the column BA_2 is excited to luminescence by a current of the order of 10 milliamps./sq. cm., there is a very marked falling off in the brightness of all the satellites, except $-0 \cdot 237$ A, which stands out as a single bright line in a group of faint lines.

These experiments show that, of the twelve components of 5461 A, all, except $-0 \cdot 237$ A, are strongly absorbed under proper conditions. The absorption of $-0 \cdot 237$ A is of quite a different order from that of the rest. It is a suggestive fact that this satellite behaves singularly in a magnetic field.*

McLennan and Ainslie have suggested that the wave-length separation of corresponding lines of two isotopes of an element may be obtained by multiplying the separation calculated on the Bohr theory by the atomic number of the element. From a consideration of calculations based on this idea, these authors and Miss Cale consider that the satellites $-0 \cdot 020$ A, $-0 \cdot 008$ A, 0, $+0 \cdot 008$ A, and $+0 \cdot 018$ A may be due to the five mercury isotopes of atomic weights 204, 202, 200, 198, and 197, and that the heavy absorption of the lines $-0 \cdot 008$ A, 0, and $+0 \cdot 008$ A may be accounted for on the ground of their being corresponding lines of the isotopes, 202, 200, and 198. It is important to consider the manner in which two lines would behave in respect of emission and absorption, if they were, in fact, corresponding lines of two isotopes. Let P and Q be two such lines. The ratio of the intensities of the radiation in these two lines from a thin layer, dx, of the luminous vapour (say $E_p\, dx$ and $E_q\, dx$, respectively) is the same as the ratio of the two sets of emitting centres. Also the ratio of A_p and A_q, the coefficients of absorption per unit thickness of the absorbing layer for the two lines is the same as the ratio of the concentrations of the absorbing centres. The radiating and absorbing atoms form always a small fraction of the total atoms present, the absorbing centres being distinct from the radiating centres on the quantum theory. In any way of exciting the vapour to radiate, the ratio of the two sets of emitting centres and that of the two sets of absorbing centres must be the same as the relative proportions of the isotopes present. That is $E_p/E_q = A_p/A_q = a$, from which $E_p/A_p = E_q/A_q$.

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* Nagaoka and Takamine, 'Phil. Mag.,' vol. 27, p. 301 (Feb., 1914).

If this relation holds, the radiation from the end of a long column of the luminous vapour should be distinguished by an equalisation of the brightness of the lines. In general, as regards emission and absorption, the real test of the similarity of the behaviour of two neighbouring lines is to be sought in the degree to which the values of E/A for the two lines approximate together. But though such similarity of behaviour is to be expected in corresponding lines of isotopes, it is not, of course, in itself, a proof of the isotopic origin of the lines.

With the idea of finding out to what extent the satellite lines tended to behave similarly we examined the radiation from the end of our long column in a spectroscope situated at a sufficient distance from the column to ensure full effectiveness from all parts of the column. The appearance presented by the lines is shown in the photograph (Plate 5, fig. 3), in which the low-pressure "long-column" spectrum (marked *b*) is contrasted with a low-pressure "thin-layer" spectrum (marked *a*). In this photograph the lines in one order are lettered correspondingly with those in the Lummer-Gehrcke diagram in fig. 3.

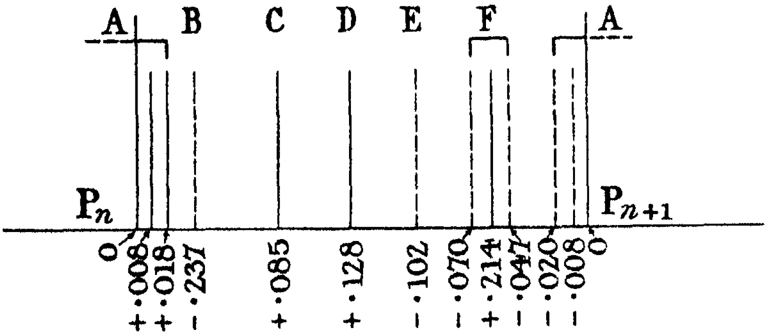

FIG. 3.

It will be noticed that, while there is a considerable relative enhancement of the weaker satellites, tending to an equality among them, they are not quite equally strong; and none of them become as strong as the (unresolved) main line group (− 0·020 A − 0·008 A, 0, + 0·008 A, + 0·018 A). An important exception is − 0·237 A, which has become as strong as the main line group itself: this brightening of − 0·237 A was only to be expected in view of the observation already made that this line is absorbed to a very slight extent under the most favourable circumstances. The relative brightness of the main line group is, of course, to be attributed to its complex character. Had the resolving power employed been sufficiently high to separate this group, each constituent would probably have appeared of the same order of brightness as the other satellites, excepting — 0·237 A.

The lack of equality in the strength of the satellites radiated from the end of our long column might have been due to the weaker lines not being quite "saturated"; it might have been possible to build up the weaker lines by further increasing the length of the column or the current density. We were able to make a test of the capability of a column of 50 cms. to produce saturation of the lines. We illuminated the whole column of 100 cms. with a current of 0·1 amp./sq. cm. and arranged to interrupt the current in the half of the column away from the spectroscope (*i.e.*, A_1B in fig. 2). Under these circumstances, if a column of 50 cms. carrying 0·1 amp./sq. cm. produces saturation in any particular line, turning on or off the other 50-cm. column will not alter the brightness of that line as seen in the spectroscope pointing along the column. As the result of these observations, carried out carefully on each satellite separately, isolating them one by one with the shutter eye-piece, we came to the conclusion that the main group was effectively saturated by the 50-cm. column; that — 0·237 A was very far from being saturated: that the remaining satellites were nearly, though not quite, saturated.

Taking this into consideration, we may fairly safely conclude that, except in the case of — 0·237 A, the ratio of E/A for the lines of the 5461 A group is fairly constant from line to line. It is therefore manifest that in this case considerations based on emission and absorption alone do not warrant us in attributing to isotopes selected satellites in preference to others which behave similarly.

In the paper already referred to by McLennan, Ainslie and Miss Cale, an experiment is described in which the radiation from one luminous column passes through a second luminous column carrying a lower current density than the first. An apparent reversal of the main group was observed, due to the heavier absorption of the central components. The authors state that "various attempts were made . . . to widen out the absorption band . . . it apparently reached a definite width, beyond which it could not be extended." From this they infer that the lines — 0·020 A and + 0·018 A are not appreciably absorbed. If these outer components are, in fact, relatively less absorbed than the inner lines, E/A for the outer lines will be greater than for the inner ones. Thus the radiation from a uniform long column should reveal an enhancement of the outer lines, resulting in an apparent reversal. A reversal of this kind was looked for by us in the radiation from the end of the 100-cm. column excited by a current of density 0·1 amp./sq. cm. No such reversal effect was observed. We conclude, therefore, that E/A is not perceptibly greater for the outer lines than for the inner lines under the conditions of our experiment. A direct experiment, showing that these outer lines are strongly absorbed, under suitable conditions, has already been described above.

The possibility of a reversal of the kind recorded by the authors cited above may be investigated thus :—

Light from a radiator Q (fig. 1) passes through an absorbing column A of length x. Let I_m and I_s represent the intensities of radiation of a main line and of each of two flanking satellites, respectively, in the radiation from the source Q : let $E_m \, . \, dx$ and $E_s \, . \, dx$ be the intensities of radiation of a layer of thickness dx in A : and let A_m and A_s be the absorption coefficients of the absorbing vapour. Then the intensities of radiation R_m and R_s of Q and A together, as viewed from a distant point on the axis of A, is given by

$$R_m = I_m e^{-A_m x} + (E_m/A_m)(1 - e^{-A_m x}),$$

and

$$R_s = I_s e^{-A_s x} + (E_s/A_s)(1 - e^{-A_s x}).$$

The condition for reversal is that the intensity of the main line shall be less than that of each satellite, *i.e.*,

$$I_s e^{-A_s x} + (E_s/A_s)(1 - e^{-A_s x}) >$$
$$I_m e^{-A_m x} + (E_m/A_m)(1 - e^{-A_m x}).$$

Now, writing k for $E_s/A_s = E_m/A_m$, and making the substitutions

$$I_m/k = n \, ; \quad I_m/I_s = b \, ; \quad \text{and } A_m/A_s = E_m/E_s = a,$$

the inequality reduces to

$$(nk/b)\, e^{-A_s x} + k\,(1 - e^{-A_s x}) >$$
$$nk \, . \, e^{-A_m x} + k\,(1 - e^{-A_m x}),$$

or,

$$(n - b)/b\,(n - 1) > e^{-x\,(A_m - A_s)}$$

i.e.,

$$(n - b)/b\,(n - 1) > e^{-A_m x\,(a-1)/a},$$

i.e.,

$$A_m x > \{a/(a - 1)\} \log \{b\,(n - 1)/(n - b)\}.$$

If $n > b$, this condition can be satisfied by suitably adjusting the length of the absorbing column (x) and the current density in it (A_m).

The reasoning is not materially affected by the fact that the main line is a close group of three.

If, as in our own experiment, the radiation from the absorbing column is negligible in comparison with that from the source Q, *i.e.*, I_m/k approaches infinity, the condition reduces to $A_m x > \{a/(a-1)\} \log b$, which is realisable. For example, take an extreme case, in which the satellite is half as bright as the main line in the radiator, while its absorption coefficient in the column is one-fifth of that of the main line. In this case it must be remembered that E_m will be five times as great as E_s. Then for the reversal effect to be seen $A_m x\ 5/4 \log_e 2 = 0 \cdot 87$. If we take $0 \cdot 26$ as the value of the coefficient of absorption for the main line and $0 \cdot 05$ as that for each flanking satellite for a current of 13 milliamps./sq. cm., as in our original experiment, then any column of greater length than $0 \cdot 87/0 \cdot 26$ cm. $= 3 \cdot 3$ cms., and carrying a current of 13 milliamps./sq. cm. will produce the effect of reversal. This reversal will be produced even though E/A is the same for the flanking satellite as for the main line. It will be seen, therefore, that an apparent reversal of this kind, produced by the relative dimming down of the main line, is no indication that E/A is greater for the satellites than for the main line. Such a reversal cannot be considered to prove the absence of absorption of the satellites.

In our previous paper we recorded an unsuccessful attempt to detect absorption in the yellow lines (5769 A and 5791 A). Under the more favourable conditions attending the use of a longer absorbing column, a higher resolving power and a source providing a widened line as a background, we have succeeded in observing the reversal of both of these, as well as of the two satellites of 5769 A ($+ 0 \cdot 044$ A and $- 0 \cdot 050$ A).

It may be observed, in this connection, that the yellow line 5791 A is the first member $1P - 2D$ of the diffuse series of singlets $1P - mD$, and the line 5769 A is the line $1P - 2d'$ of the combination series $1P - md'$; hence the absorbing centres are the same for both these lines according to the quantum theory, and are atoms in the state 1P. These atoms are the radiators of the line $1P - 1S$, *i.e.*, of 1849 A. This would lead one to expect that the experimental conditions which would show the reversal of one line would also exhibit the reversal of the other. The fact (observed by Pflüger) that the brighter line 5790 A has a coefficient of absorption less than that of 5769 A is to be accounted for by the complex character of the former line, in which the main constituent is accompanied by close lines, which, like $- 0 \cdot 237$ A of the green line, are comparatively feebly absorbed.

It is of interest to note that in the course of this part of our work we observed in the light radiated by the long column the satellite $- 0 \cdot 112$ A of the line 5769 A, recorded originally by Janicki, and since seen by Wood and Nagaoka.

Gale and Lemon, using a large Michelson grating, failed to find this satellite on their photographs. We found that the satellite could not be detected in the light of an ordinary low-pressure arc carrying a current of 4 amps./sq. cm.; whereas it was clearly seen in the light radiated from the end of the long column carrying a current density as low as 0·06 amp./sq. cm. This emphasises the utility of long columns as radiators for the study of weak lines. The satellite now referred to is very diffuse, compared with the two others belonging to 5769 A.

We are continuing the work with the lines $1p_2 - 1s$ and $1p_3 - 1s$, and have been able to reverse four satellites of the former line.

Summary.

1. The absorption of the components of the 5461 A group $1p_1 - 1s$ by luminous mercury vapour has been examined, with the aid of a Lummer-Gehrcke plate and an absorbing column 100 cms. long. All the satellites were found to be strongly absorbed, under suitable conditions, with the exception of − 0·237 A, which was also absorbed, but to a much less degree. The ratio of emission to absorption is found to be fairly constant for all the lines, except − 0·237 A. All the resolved satellites, except − 0·237 A, have been reversed on a continuous bright background. The conditions for reversal are discussed. The bearing of these results on the possible isotopic origin of some of the satellites is considered.

2. The absorption and reversal of the lines 5769 A $1P - 2d'$ and 5791 A $1P - 2D$, for which the absorption centres are the same and in the state 1P, have been observed. Two satellites of 5769 A (0·044 A and − 0·050 A) have been reversed.

3. The effectiveness of long columns as radiators of weak lines is brought out by the observation of the feeble satellite − 0·112 A of 5679 A, in the light radiated from the end of a 100-cm. column carrying a current of 0·06 amp./sq. cm.

A Spherical Source in a Rotating Liquid.

By S. F. Grace, University of Liverpool.

(Communicated by Prof. G. I. Taylor, F.R.S. Received February 19, 1924.)

§ 1. The author has already discussed the solutions of two problems dealing with the free motion of a sphere in a rotating liquid.* In connection with these, it was suggested that one of the simplest problems with rotating liquids might be that in which a point-source is placed on the axis. In such a problem, however, the conditions for small motion are violated at points near the source, so that it was decided to replace the point-source by a spherical source, this being defined as a uniform normal discharge of liquid from the surface of a sphere of finite radius. It was hoped that the solution of this problem might throw light on that of others and in particular on the one in which a sphere is towed through the liquid with relatively constant velocity.

Consider, therefore, a liquid rotating about an axis like a rigid body, and suppose that, at a given instant, a spherical source is suddenly generated relative to the rotating liquid, and then maintained, the centre of the source being on the axis. The problem is to determine the motion of the liquid at any subsequent time on the assumption that the motion is small, that is, such that squares and products of velocity and vorticity-components may be neglected. This subsequent motion will be symmetrical with respect to the axis.

The solution of the problem shows that the motion of the liquid along the axis is always away from the sphere. At a particular point the velocity oscillates with constant amplitude about a value equal to the velocity of discharge from the sphere: this amplitude is zero at the sphere, but increases with the distance from the sphere until, at infinity, its value is equal to the velocity of discharge. The period of the oscillation decreases from an infinitely large value at the sphere to zero at infinity.

The plane through the centre of the spherical source perpendicular to the axis of rotation will be termed the equatorial plane. The liquid has no motion across this plane. The motion in the plane at any particular time depends only on the distance from the centre of the sphere and expressions for the radial and transverse components of velocity with respect to the centre have been obtained. From these expressions it is seen that the motion tends rapidly to zero away from the sphere, thus exhibiting a characteristic already noted in previous problems (*loc. cit.*). At a particular point the radial component of velocity tends to zero as time increases, oscillating about the zero value with continually diminishing amplitude; the transverse component of velocity is opposite to the direction of rotation of the liquid and tends to become constant at a particular point. Thus the paths of particles in the equatorial plane tend to become concentric circles, the centre being at the centre of the sphere. The motion becomes increasingly violent at the sphere itself, but, on examination, this violent motion at the spherical source is found to take place only in the neighbourhood of the equatorial plane. The fact that the increasingly violent motion does exist, however, means that the solution will only represent the actual motion of the liquid for a restricted time.

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* "Free Motion of a Sphere in a Rotating Liquid parallel to the Axis of Rotation," 'Roy. Soc. Proc.,' A, vol. 102 (1922); "Free Motion of a Sphere in a Rotating Liquid at Right Angles to the Axis of Rotation," 'Roy. Soc. Proc.,' A, vol. 104 (1923).

The results indicate that the flow of liquid, due to the discharge from the sphere, is drawn out in the direction of the axis.

The discussion will be considerably curtailed by referring to the previous papers already cited. Reference to the first paper is made by placing (A) after the reference; reference to the second by placing (B) after the reference.

Mathematical Problem.

§2. Take Cartesian axes $Oxyz$ rotating about Oz with constant angular velocity ω, and let the centre of the spherical source be at the origin. Equations 1, 3, 4 of §2 (A) hold, but the boundary condition is

$$(lu + mv + nw)_{r=a} = \mathrm{W},$$

where l, m, n are the direction cosines of the normal to the sphere, a the radius of the sphere, W the velocity of discharge.

Let

$$u = \sum_{s=0}^{\infty} u_s \frac{(2\omega t)^s}{s!}, \quad v = \sum_{s=0}^{\infty} v_s \frac{(2\omega t)^s}{s!}, \quad w = \sum_{s=0}^{\infty} w_s \frac{(2\omega t)^s}{s!},$$

$$\mathrm{P} = 2\omega \sum_{s=0}^{\infty} \mathrm{P}_s \frac{(2\omega t)^s}{s!},$$

as in §2 (A), then equation 5 (A) holds and the boundary condition is

$$(lu_0 + mv_0 + nw_0)_{r=a} = \mathrm{W}, \quad (lu_s + mv_s + nw_s)_{r=a} = 0, \qquad s > 0.$$

Equations 6 (A), 7 (A) and the expressions for u, v, w in terms of P_s follow.

If now r, θ, ϕ are the spherical polar co-ordinates of x, y, z, the velocity-potential of the initial motion, P_{-1}, is given by

$$P_{-1} = Wa^2/r,$$

and, if $\lambda = a/r$,

$$u_0 = W\lambda^2 \sin\theta\cos\phi, \quad v_0 = W\lambda^2 \sin\theta\sin\phi, \quad w_0 = W\lambda^2\cos\theta.$$

Hence, as in §2 (A),

$$\nabla^2 P_0 = 0, \qquad \nabla^2 P_s = -\frac{\partial^2 P_{s-2}}{\partial z^2}, \qquad s > 0.$$

The symmetry of the disturbance with respect to the axis ensures that P_s is independent of ϕ and the boundary condition becomes

$$\left(\frac{\partial P_0}{\partial r}\right)_{r=a} = 0, \qquad \left(\frac{\partial P_1}{\partial r}\right)_{r=a} = -W - \cos\theta\left(\frac{\partial P_{-1}}{\partial z}\right)_{r=a},$$

$$\left(\frac{\partial P_s}{\partial r}\right)_{r=a} = -\cos\theta\left(\frac{\partial P_{s-2}}{\partial z}\right)_{r=a}, \qquad s > 1.$$

It follows that P_0 is zero, and generally that

$$P_{2s} = 0, \qquad s \geqslant 0.$$

Hence the problem reduces to finding a sequence of functions P_{2s+1}, $(s \geqslant 0)$, which satisfy

$$\nabla^2 P_{2s+1} = -\frac{\partial^2 P_{2s-1}}{\partial z^2}, \qquad s \geqslant 0, \tag{8}$$

$$\left(\frac{\partial P_1}{\partial r}\right)_{r=a} = -W - \cos\theta\left(\frac{\partial P_{-1}}{\partial z}\right)_{r=a}, \quad \left(\frac{\partial P_{2s+1}}{\partial r}\right)_{r=a} = -\cos\theta\left(\frac{\partial P_{2s-1}}{\partial z}\right)_{r=a}, \quad s > 0.$$

The Solution.

§3. Starting with $P_{-1} = Wa^2/r$, and obtaining the functions P_{2s+1} $(s \geqslant 0)$, step by step, by assuming a particular integral of (8) and then satisfying the boundary condition through the introduction of appropriate harmonic functions, it is found that

$$P_{2s+1} = \left(1 + \frac{a^2\nabla^2}{3!} + \frac{a^4\nabla^4}{5!} + \ldots + \frac{a^{2s+2}\nabla^{2s+2}}{(2s+3)!}\right) F_{2s+1}(r, \theta), \tag{9}$$

where

$$F_{2s+1}(r, \theta) = (-)^s \frac{Wa^2}{r} \frac{1.3.\ldots(2s+1)}{2.4.\ldots(2s+2)}\left(\frac{2s+2}{2s+1}\sin^{2s}\theta - \sin^{2s+2}\theta\right).$$

This may be written in the extended form

$$\mathrm{P}_{2s+1} = \mathrm{W}a \sum_{m=0}^{s+1} \lambda^{2m+1} \mathrm{D}_{2m,2s}(\theta),$$

where

$$\mathrm{D}_{2m,2s}(\theta) = (-)^{s-m+1} \frac{(2m+1)(2m+3)\ldots(2s+2m+1)}{2^{s+1}\,.\,m!\,(s-m+1)!} \frac{1}{2m+1} \times$$

$$\Big[\sin^{2s+2}\theta - {}^{m}\mathrm{C}_1 \frac{2s+2}{2s+2m+1} \sin^{2s}\theta$$

$$+ {}^{m}\mathrm{C}_2 \frac{(2s+2)\,2s}{(2s+2m+1)(2s+2m-1)} \sin^{2s-2}\theta - \ldots$$

$$\ldots + (-)^{m} \frac{(2s+2)\,2s\ldots(2s-2m+4)}{(2s+2m+1)(2s+2m-1)\ldots(2s+3)} \sin^{2s-2m+2}\theta$$

$$- \frac{2s-2m+2}{2s+2m+1} \Big\{ \sin^{2s}\theta - {}^{m}\mathrm{C}_1 \frac{2s}{2s+2m-1} \sin^{2s-2}\theta + \ldots$$

$$\ldots + (-)^{m} \frac{2s(2s-2)\ldots(2s-2m+2)}{(2s+2m-1)(2s+2m-3)\ldots(2s+1)} \sin^{2s-2m}\theta \Big\} \Big],$$

for $s \geqslant 0$, and it may be noted that

$$(2s+3)\,\mathrm{D}_{2s+2,2s}(\theta) = (-)^{s+1}\,\mathrm{P}^{0}{}_{2s+2}(\cos\theta),$$

$\mathrm{P}^{0}{}_{2s+2}(\cos\theta)$ denoting Legendre's function.*

Verification.

§ 4. The expression (9) satisfies

$$\nabla^2 \mathrm{P}_{2s+1} = -\frac{\partial^2 \mathrm{P}_{2s-1}}{\partial z^2}, \qquad s > 0,$$

provided

$$\nabla^2 \mathrm{F}_{2s+1}(r, \theta) = -\frac{\partial^2 \mathrm{F}_{2s-1}(r, \theta)}{\partial z^2},$$

and, on examination, this is found to be true. Further

$$\nabla^2 \mathrm{P}_1 = -\frac{\partial^2 \mathrm{P}_{-1}}{\partial z^2}.$$

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* *March 10, 1924.*—A referee points out that $\mathrm{D}_{2m,2s}(\theta)$ is always expressible by generalised Legendre functions; the formula in Ferrer's notation (Whittaker & Watson, 'Modern Analysis,' p. 323), is

$$2^{s-m+1}(2m+1)(s-m+1)!\ \mathrm{D}_{2m,2s}(\theta)$$

$$= (-)^{s+1} \sin^{s-m}\theta \left\{ \sin\theta \,.\, \mathrm{P}_{s+m+1}^{s-m+1}(\cos\theta) - (2s-2m+2)\,\mathrm{P}_{s+m}^{s-m}(\cos\theta) \right\}.$$

It remains to show that the assumed form of P_{2s+1} satisfies the boundary condition. Taking

$$\left(\frac{\partial P_{2s+1}}{\partial r}\right)_{r=a} = -W\sum_{m=0}^{s+1}(2m+1)\,D_{2m,2s}(\theta),$$

and considering separately the expressions due to the two terms in $F_{2s+1}(r,\theta)$, it is found that

$$\left(\frac{\partial P_{2s+1}}{\partial r}\right)_{r=a} = -W\sum_{k=0}^{s+1}(-)^k\,{}^{s+1}C_k\sin^{2s-2k+2}\theta - W\sum_{k=0}^{s}(-)^k\,{}^{s}C_k\sin^{2s-2k}\theta$$

$$= -W\sin^2\theta\,(\sin^2\theta-1)^s. \qquad (10)$$

Now

$$\left(\frac{\partial P_{2s+1}}{\partial \theta}\right)_{r=a} = Wa\sum_{m=0}^{s+1}\frac{dD_{2m,2s}(\theta)}{d\theta},$$

and, on examination, it is found that this is zero. Hence since

$$-\cos\theta\left(\frac{\partial P_{2s-1}}{\partial z}\right)_{r=a} = -\cos^2\theta\left(\frac{\partial P_{2s-1}}{\partial r}\right)_{r=a} + \frac{\cos\theta\sin\theta}{a}\left(\frac{\partial P_{2s-1}}{\partial \theta}\right)_{r=a}$$

$$= -W\sin^2\theta\,(\sin^2\theta-1)^s, \qquad s>0,$$

and

$$\left(\frac{\partial P_1}{\partial r}\right)_{r=a} = -W - \cos\theta\left(\frac{\partial P_{-1}}{\partial z}\right)_{r=a},$$

the boundary condition is seen to be satisfied.

The convergence of the series for u, v, w and P in terms of P_s follows, exactly as in § 5 (A), for all finite values of t, since it can be shown that

$$\frac{|P_{2s+1}|}{(2s+1)!} < \frac{8Wa}{(s+1)!},$$

and it is now proposed to proceed to a discussion of the results.

Velocity of the Liquid along the Axis.

§ 5. On the axis, θ is zero or π, but in view of the symmetry of the disturbance, it is only necessary to consider $\theta = 0$. Now

$$w_{2s+1} = -\frac{\partial P_{2s}}{\partial z} = 0,$$

$$w_{2s} = -\left(\frac{\partial P_{2s-1}}{\partial z}\right)_{\theta=0} = -\left(\frac{\partial P_{2s-1}}{\partial r}\right)_{\theta=0}$$

$$= W\sum_{m=0}^{s}(2m+1)\,\lambda^{2m+2}D_{2m,2s-2}(0).$$

But

$$D_{2m,\,2s-2}(0) = 0, \qquad m < s-1,$$

$$(2s-1)\,D_{2s-2,\,2s-2}(0) = (-1)^{s-1}, \qquad (2s+1)\,D_{2s,\,2s-2}(0) = (-1)^{s}.$$

Hence

$$w_{2s} = (-)^{s-1}\,W\,(\lambda^{2s} - \lambda^{2s+2}), \qquad s > 0,$$

and

$$w_0 = W\lambda^2.$$

Consequently

$$w = W\lambda^2 + \sum_{s=1}^{\infty} (-)^{s-1}\,W\,(\lambda^{2s} - \lambda^{2s+2})\,(2\omega t)^{2s}/(2s)!$$

$$= W - W\,(1-\lambda^2)\cos 2\lambda\omega t,$$

and

$$u = v = 0.$$

Diagram I indicates the variation of the function w with r and t; the values of w/W are plotted against those of $r/a = 1/\lambda$, and the separate curves 0, 1, 2, ... 10 correspond respectively to $2\omega t = 0, 1, 2, \ldots 10$; $2\omega t = 10$ is roughly equivalent to $t = 0{\cdot}8T$, where T is the period of a complete rotation of the undisturbed liquid.

It is seen that the motion along the axis is always away from the sphere; the velocity at any particular point oscillates about the value W with amplitude $W(1-\lambda^2)$ and period $2\pi/2\lambda\omega = T/2\lambda$.

Velocity of the Liquid over the Equatorial Plane.

§ 6. On the equatorial plane, $\theta = \frac{1}{2}\pi$, and

$$w = 0.$$

From equations 7 (A) it is seen that

$$u_{2s+1} + u_{2s-1} = -\frac{\partial P_{2s-1}}{\partial y} = -\sin\phi\left(\frac{\partial P_{2s-1}}{\partial r}\right)_{\theta=\frac{1}{2}\pi}, \qquad s > 0,$$

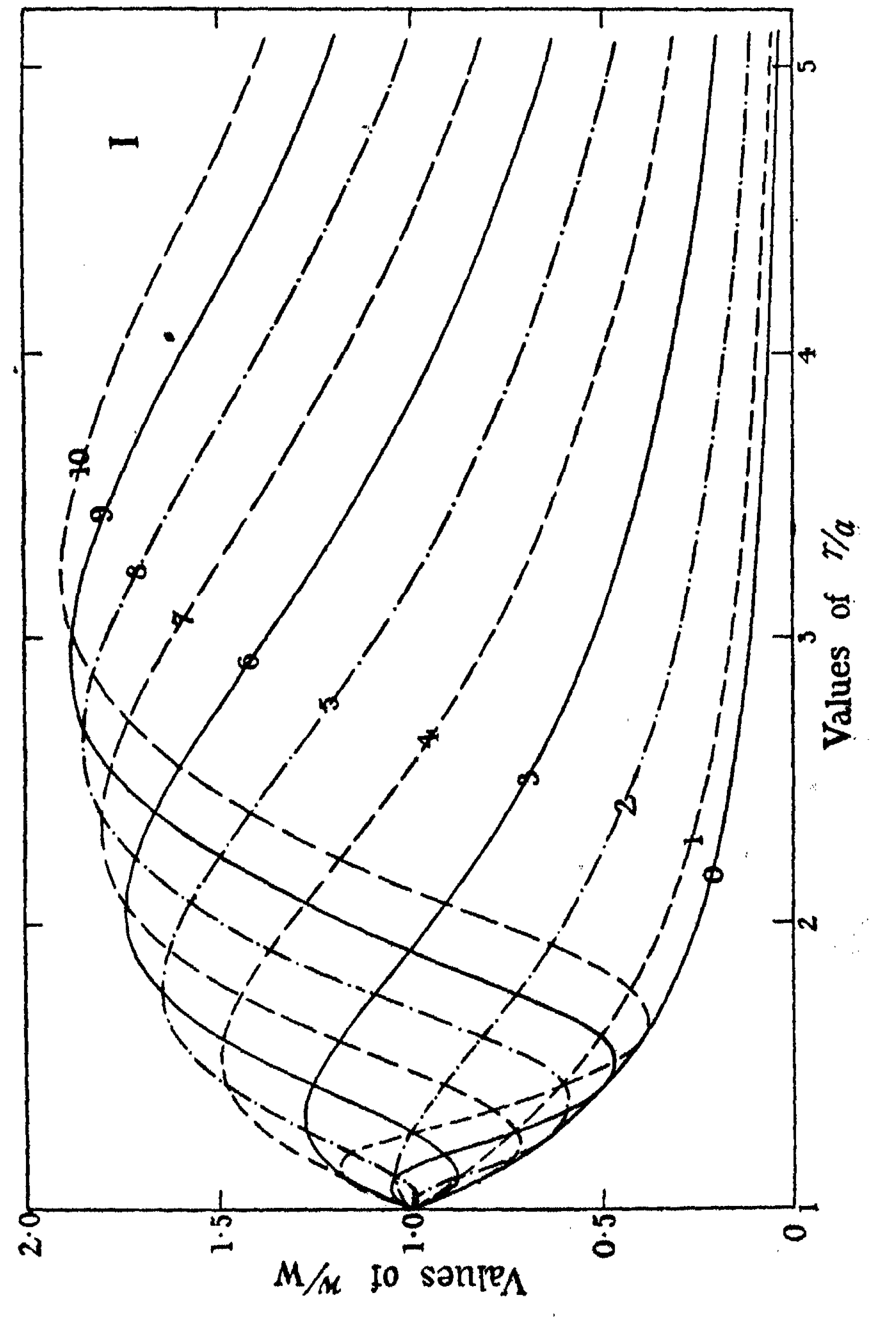
$$= -W\sin\phi \sum_{m=0}^{s} (2m+1)\,\lambda^{2m+2}\,D_{2m,\,2s-2}(\tfrac{1}{2}\pi).$$

Evaluating $D_{2m,\,2s-2}(\frac{1}{2}\pi)$, $s > 0$, we find that

$$1 - {}^{m}C_1\,\frac{2s}{2s+2m-1} + {}^{m}C_2\,\frac{2s\,(2s-2)}{(2s+2m-1)\,(2s+2m-3)} - \ldots$$

$$\ldots + (-)^m\,\frac{2s\,(2s-2)\ldots(2s-2m+2)}{(2s+2m-1)\,(2s+2m-3)\ldots(2s+1)}$$

$$= \frac{1\,.\,3\,.\,\ldots(2m-1)}{(2s+1)\,(2s+3)\ldots(2s+2m-1)}, \qquad m > 0.$$


I
Values of w/W
2·0
1·5
1·0
0·5
0
Values of r/a
1
2
3
4
5
0
1
2
3
4
5
6
7
8
9
10

Hence

$$(2m+1)\,\mathrm{D}_{2m,\,2s-2}\left(\tfrac{1}{2}\pi\right) = (-)^{s-m}\frac{1\,.\,3\,.\,\ldots\,(2s-1)}{2^s\,.\,m\,!\,(s-m)\,!}\,\frac{2m-1}{2s-1}, \qquad m \geqslant 0,$$

and

$$\sum_{m=0}^{s}(-)^{s-m}\lambda^{2m+2}\frac{1\,.\,3\,.\,\ldots\,(2s-1)}{2^s\,.\,m\,!\,(s-m)\,!}\,\frac{2m-1}{2s-1}$$

$$= (-)^s\frac{1\,.\,3\,.\,\ldots\,(2s-1)}{2\,.\,4\,.\,\ldots\,2s}\,\frac{1}{2s-1}\sum_{m=0}^{s}(-)^m\,{}^s\mathrm{C}_m\,(2m-1)\,\lambda^{2m+2},$$

so that, $s > 1$,

$$u_{2s+1} + u_{2s-1} = \mathrm{W}\sin\phi\left\{(-)^s\frac{1\,.\,3\,.\,\ldots\,(2s-1)}{2\,.\,4\,.\,\ldots\,2s}\,\lambda^2(1-\lambda^2)^s\right.$$

$$\left.+\,(-)^{s-1}\frac{1\,.\,3\,.\,\ldots\,(2s-3)}{2\,.\,4\,.\,\ldots\,(2s-2)}\,\lambda^2(1-\lambda^2)^{s-1}\right\}.$$

Since $u_3 = -\tfrac{1}{2}\mathrm{W}\lambda^2(1-\lambda^2)\sin\phi$, it follows that

$$u_{2s+1} = (-)^s\,\mathrm{W}\sin\phi\,\frac{1\,.\,3\,.\,\ldots\,(2s-1)}{2\,.\,4\,.\,\ldots\,2s}\,\lambda^2(1-\lambda^2)^s = v_{2s}, \qquad s > 0,$$

and

$$u_1 = \mathrm{W}\lambda^2\sin\phi = v_0.$$

Similarly

$$v_{2s+1} + v_{2s-1} = \frac{\partial \mathrm{P}_{2s-1}}{\partial x} = \mathrm{W}\cos\phi\left(\frac{\partial \mathrm{P}_{2s-1}}{\partial r}\right)_{\theta=\frac{1}{2}\pi},$$

so that

$$v_{2s+1} = (-)^{s+1}\,\mathrm{W}\cos\phi\,\frac{1\,.\,3\,.\,\ldots\,(2s-1)}{2\,.\,4\,.\,\ldots\,2s}\,\lambda^2(1-\lambda^2)^s = -\,u_{2s}, \qquad s > 0,$$

$$v_1 = -\,\mathrm{W}\lambda^2\cos\phi = -\,u_0.$$

If now u', v' denote respectively the radial and transverse components of the velocity of the liquid in the equatorial plane, then

$$u'_{2s+1} = 0, \qquad s > 0,$$

$$u_0' = \mathrm{W}\lambda^2, \quad u_{2s}' = (-)^s\frac{1\,.\,3\,\ldots\,.\,(2s-1)}{2\,.\,4\,.\,\ldots\,2s}\,\mathrm{W}\lambda^2(1-\lambda^2)^s, \qquad s > 0,$$

and

$$v_1' = -\mathrm{W}\lambda^2, \quad v_{2s+1}' = (-)^{s+1}\frac{1\,.\,3\,.\,\ldots\,(2s-1)}{2\,.\,4\,.\,\ldots\,2s}\,\mathrm{W}\lambda^2(1-\lambda^2)^s, \qquad s > 0$$

$$v_{2s}' = 0, \qquad s \geqslant 0.$$

Hence

$$u' = \mathrm{W}\lambda^2 + \sum_{s=1}^{\infty}(-)^s\,\mathrm{W}\lambda^2\,\frac{1\,.\,3\,.\,\ldots\,(2s-1)}{2\,.\,4\,.\,\ldots\,2s}\,\frac{\{2\omega t\sqrt{(1-\lambda^2)}\}^{2s}}{2s\,!}$$

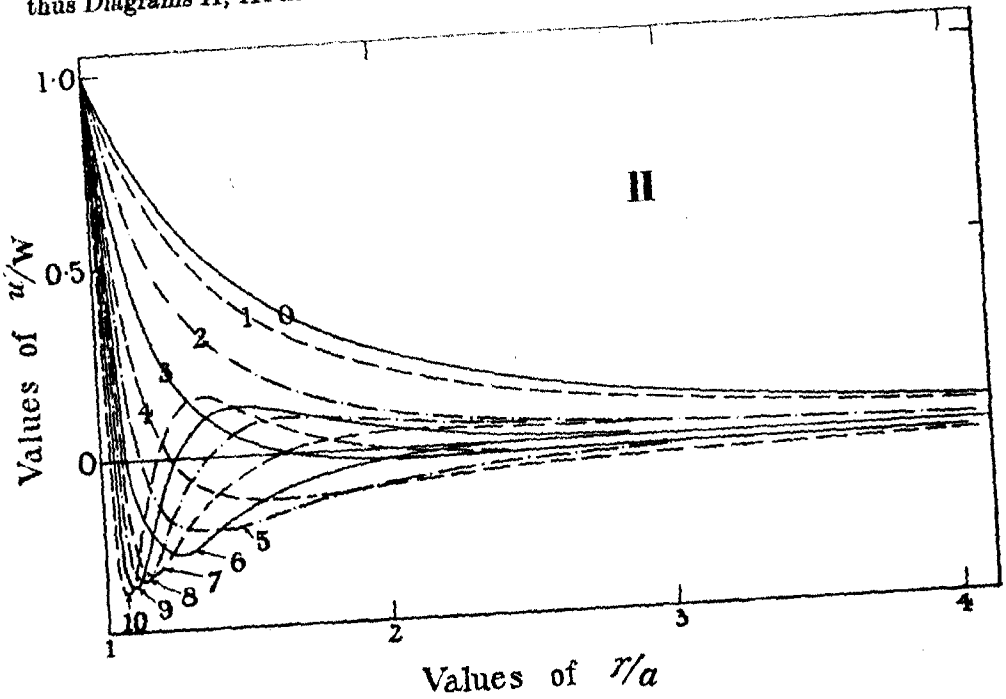
$$= \mathrm{W}\lambda^2\,.\,\mathrm{J}_0\{2\omega t\sqrt{(1-\lambda^2)}\},$$

and

$$v' = -W\lambda^2 \, . \, 2\omega t + \Sigma_{s=1}^{\infty} (-)^{s+1} \frac{1 \, . \, 3 \, \ldots . \, (2s-1)}{2 \, . \, 4 \, \ldots . \, 2s} W\lambda^2 (1-\lambda^2)^s \frac{(2\omega t)^{2s+1}}{(2s+1)\,!}$$

$$= -W \frac{\lambda^2}{\sqrt{(1-\lambda^2)}} \int_0^{2\omega t \sqrt{(1-\lambda^2)}} J_0(x) \, dx.$$

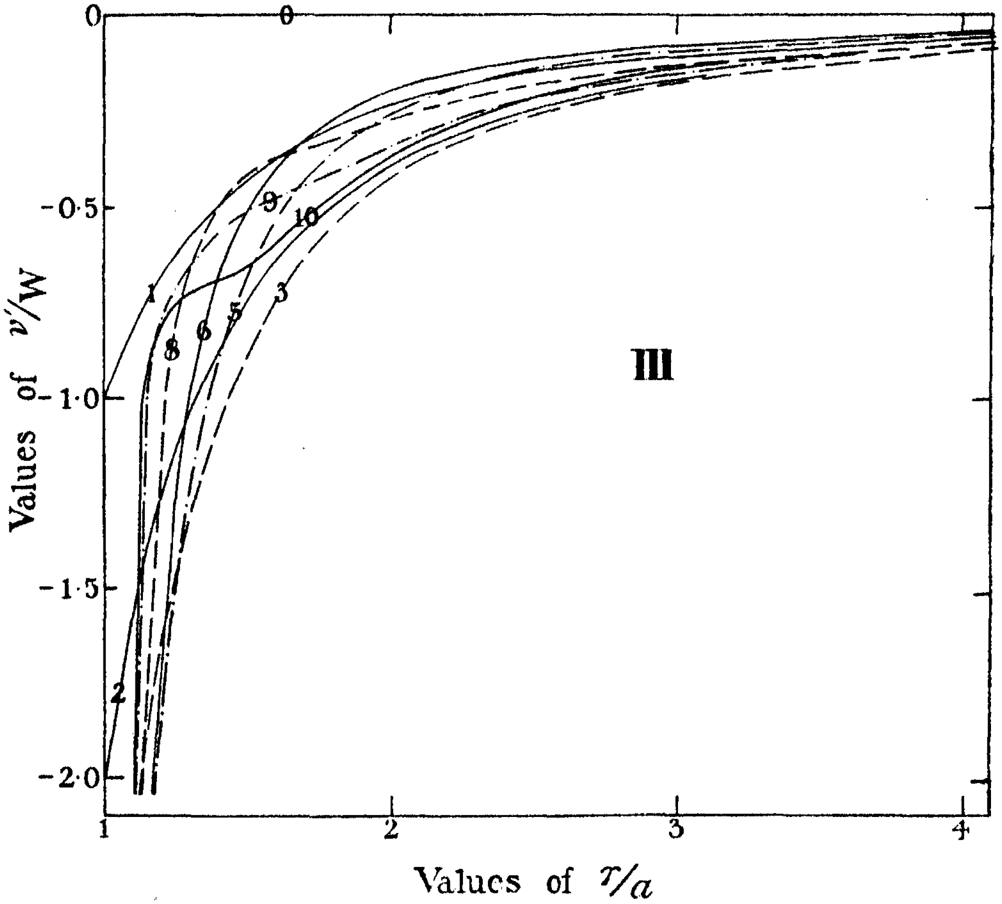
The method of exhibiting these results is similar to that already employed; thus Diagrams II, III have been drawn to represent the variations of u', v' with r and t; the various curves represent the variation of u', v' with r at the instants given by $2\omega t = 0, 1, 2, \ldots 10$. In Diagram III the curves corresponding to $2\omega t = 4, 7$ have been omitted in order not to cause undue complication.



It is observed that the velocity tends rapidly to zero as we proceed away from the sphere. Taking a constant value of λ ($\neq 1$), it is seen that as the time increases the value of u' oscillates about the zero value, with continually diminishing amplitude, whereas the value of v' oscillates in a similar manner about a definite finite value. Thus, as time increases, the motion in the equatorial plane tends to become circular; and, in fact, as $t \to \infty$

$$u' \to 0, \qquad v' \to -W\lambda^2/\sqrt{(1-\lambda^2)}.$$

At the spherical source u is constant and equal to W, but $v' = -\mathrm{W} \cdot 2\omega t$, and consequently tends to become infinite with time. This latter fact, as well as the fact that gradients of velocity tend to become infinite, means that the solution of the problem has only a physical application for a restricted time.



It is interesting to compare the Diagrams II, III with VI, VII, VIII (B), all of which refer to the liquid motion in the equatorial plane. Diagram IV (A) refers to the motion across this plane. A great similarity is noted to exist between the various diagrams.

Velocity of the Liquid at the Spherical Source.

§ 7. We now examine the velocity for $r = a$.

Expressing the equations 3 (A) in spherical polar co-ordinates, we obtain

$$\begin{aligned} &\frac{\partial u'}{\partial t} - 2\omega v' \sin\theta = -\frac{\partial \mathrm{P}}{\partial r}, \\ &\frac{\partial v'}{\partial t} + 2\omega u' \sin\theta + 2\omega w' \cos\theta = 0, \qquad (12) \\ &\frac{\partial w'}{\partial t} - 2\omega v' \cos\theta = -\frac{\partial \mathrm{P}}{r\,\partial\theta}, \end{aligned}$$

where u' denotes the radial velocity of the liquid, v' the transverse velocity (ϕ increasing) and w' the meridional velocity (θ increasing).

Now on $r = a$, we have

$$u' = \mathrm{W},$$

so that

$$2\omega v' \sin\theta = \left(\frac{\partial \mathrm{P}}{\partial r}\right)_{r=a}.$$

From (10)

$$\left(\frac{\partial \mathrm{P}_{2s+1}}{\partial r}\right)_{r=a} = -\mathrm{W}\sin^2\theta\,(\sin^2\theta - 1)^s,$$

hence

$$v_{2s+1}{}' = (-)^{s+1}\,\mathrm{W}\sin\theta\cos^{2s}\theta,$$

and it follows that

$$v' = -\mathrm{W}\tan\theta\sin(2\omega t\cos\theta).$$

The equation (12) now gives

$$w' = -\mathrm{W}\tan\theta\,\{1 - \cos(2\omega t\cos\theta)\},$$

so that the motion at the spherical source only tends to become violent in the neighbourhood of the equatorial plane.

§ 8. Consider the results obtained by making $\mathrm{W} \to \infty$ and $a \to 0$ in such a way that $\mathrm{W}a^2$ remains finite and equal to M, say. The problem reduces to finding P_{2s+1}, $s \geqslant 0$, such that

$$\begin{aligned} \nabla^2 \mathrm{P}_{2s+1} &= -\frac{\partial^2 \mathrm{P}_{2s-1}}{\partial z^2}, \qquad s \geqslant 0, \\ \iint \frac{\partial \mathrm{P}_{2s+1}}{\partial r}\,d\mathrm{S} &= -\iint \cos\theta\,\frac{\partial \mathrm{P}_{2s-1}}{\partial z}\,d\mathrm{S}, \qquad s > 0, \\ \iint \frac{\partial \mathrm{P}_1}{\partial r}\,d\mathrm{S} &= -4\pi\mathrm{M} - \iint \cos\theta\,\frac{\partial \mathrm{P}_{-1}}{\partial z}\,d\mathrm{S}, \end{aligned}$$

the integral being taken over a sphere of radius r, and $\mathrm{P}_{-1} = \mathrm{M}/r$.

The solution is $s \geqslant 0$,

$$P_{2s+1} = (-)^s \frac{M}{r} \cdot \frac{1 . 3 . \ldots (2s+1)}{2 . 4 . \ldots (2s+2)} \left\{ \frac{2s+2}{2s+1} \sin^{2s}\theta - \sin^{2s+2}\theta \right\},$$

and, using the notation of the previous section, it is found that

$$u' = \{J_0(2\omega t \sin\theta) + 2\omega t \cos\theta \cot\theta . J_1(2\omega t \sin\theta)\} M/r^2,$$

$$v' = \left\{ 2\omega t \cos\theta \cot\theta . J_0(2\omega t \sin\theta) - \operatorname{cosec}^2\theta \int_0^{2\omega t \sin\theta} J_0(x)\, dx \right\} M/r^2,$$

$$w' = 0.$$

Except for $\theta = 0$, $\frac{1}{2}\pi$, π, the expressions for u', v' tend to become infinite with t for any value of r. An attempt is being made, however, starting from this solution, to obtain, by a method involving successive approximations, a complete solution of the problem in which a point-source is suddenly generated on the axis of a rotating liquid, that is, a solution which is not restricted to small motion. Preliminary work has already been effected, but whether or not the attempt will be successful is as yet problematical.

The author wishes to express his thanks to Prof. J. Proudman for his interest in the work and for the various suggestions he has made, also to Prof. G. I. Taylor. The present paper owes its inception to the suggestion made by Prof. G. I. Taylor that the author should consider what would happen if a point-source were placed on the axis of a rotating liquid.

Experiments on the Duration of Impacts, Mainly of Bars with Rounded Ends, in Elucidation of the Elastic Theory.

By J. E. P. Wagstaff, M.A., Fellow of St. John's College, Cambridge, Lecturer in Physics in the University of Leeds.

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The general theory of impact enunciated by Newton divides bodies into two classes, " perfectly elastic " and " imperfectly elastic." In the former class, no sensible dissipation of energy occurs during impact, while in the latter a certain proportion of the energy of the relative motion is always dissipated ultimately into heat. Many actual bodies are not far from being perfectly elastic in the Newtonian sense.

For the theoretical discussion of the problem, we have at our disposal two distinct mathematical theories applicable mainly under different conditions, due to Hertz and St. Venant. The Hertz theory, which regards impact as a statical effect, rests on the foundation that when two bodies are pressed steadily together, they come into contact over a small area and that intense stress is developed in the bodies locally around it, rapidly falling off at a distance. The creation of a state of strain is accomplished by wave propagation, but each stage of the compression is so slow that infinitesimal waves have time to adjust it locally without drawing away any sensible fraction of the energy.

Hertz tests the statical character of his impacts by assuming it is so, and calculating the circumstances of the impact on that basis. The test that the hypothesis is justified is that the time of impact should work out large compared with the time a wave takes to traverse the body and back again. Under such conditions the adjusting waves can never mount up to finite value. In the case of short bodies, the impact is thus determined by the form of the surfaces near the contact, and by the total momentum transferred there. It depends on the relative motion of the bodies and their masses, but the form of the bodies at a distance from the place of contact is immaterial.

The calculation of the Hertz impact implies also that the region of perfect resilience is not overstepped, and experiment will test how far that hypothesis may be pushed. The other impact problem of different scope, developed long previously by St. Venant (1867), is the impact of two bars, flat end to flat end, if that can be sufficiently accomplished. In long bars finite waves are thus set up which run backwards and forwards with successive reflections so that the circumstances of the impact, now a kinetic problem, may be very complex, involving the lengths of the bars. The actual impact of shorter rods is an intermediate phenomenon.

The working of the Hopkinson pressure-bar* seems to be directly involved in the theory, as depending on the conditions under which a sudden local pressure at one end gathers itself up at a short distance into a travelling wave uniform across the section. The following experiments are intended to test the extent to which these two theoretical types of impact are borne out in fact, and to examine the range of transition between them. References to the cardinal sources in the literature of this subject are given below.†

Description of Apparatus.

The method used for measuring time of impact depends on the known rate of discharge of a condenser C through a circuit of resistance R and inductance L. Hamburger‡ and others measured these short intervals by finding the amount of electricity that passes through the circuit from a battery of cells during the time impact lasts. In the present experiments a condenser has taken the place of a battery, first because it is the simplest kind of battery possible, and secondly as it possesses the additional advantage that over short intervals of time, it is not so liable to be masked by polarization such as may enter in the case of cells where the liberation of electrical energy depends on chemical change. The apparatus is shown diagrammatically in figs. 1 and 2. A condenser C is charged up from a battery B by inserting the plug P, the bars A of equal length being kept apart during this operation by the contrivance shown in fig. 2. In parallel with this condenser is the circuit containing two freely suspended steel bars with rounded ends, in series with a resistance box and ballistic galvanometer through which the condenser can discharge itself whenever the bars are in contact. The bars are fitted with small hooks S, coated with sealing wax to ensure good insulation, to which are attached the thin suspensions. These are fully two metres long, and the farther ends are fastened to adjustable supports screwed to very stout cross-beams (fig. 3). The supports sketched in fig. 5 are capable of very fine adjustment, one complete turn of the screw releasing only 1 mm. of suspension. This is very essential in this type of experiment, as perfect alignment of the bars is one of the most important requirements. The bars are placed in electrical communication with the rest of the circuit by the leads P. The connecting wires, coiled as shown in fig. 2, so as not to hinder the free motion of the bars, are held between the nuts N. E is a thin tube of ebonite to ensure complete insulation when the bar is picked up after one impact. The picking-up device is shown in fig. 4 and requires no further explanation. The dropping apparatus is shown in figs. 2 and 2A.

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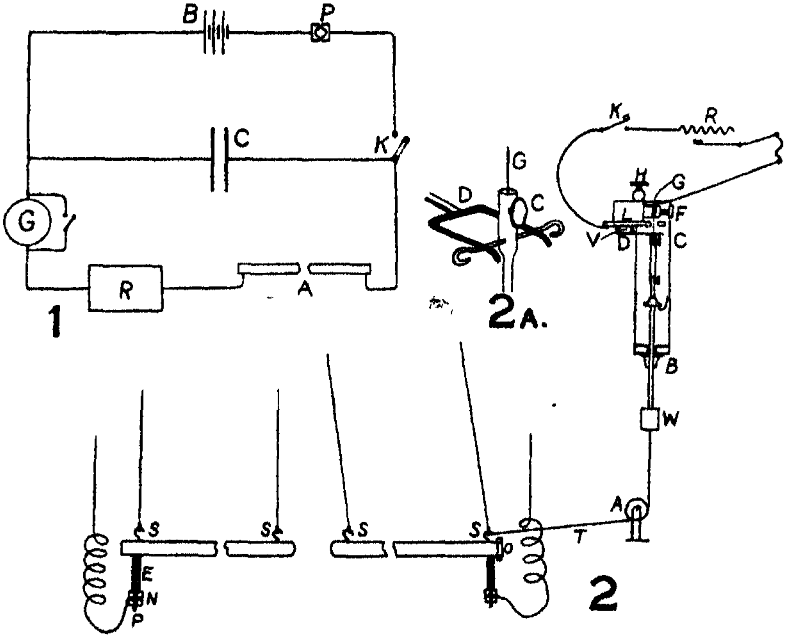
* B. Hopkinson, 'Phil. Trans.,' A, 1913-14; or 'Collected Papers.'

† Hertz, 'Crelle's Journal für Math.,' vol. 92 (1881), or 'Miscellaneous Papers,' English Ed., p. 146; Saint Venant, 'Liouville's J. de Math.' (Sér. 2), vol. 12 (1867); Voigt, 'Wied. Ann.,' vol. 19 (1883); Sears, 'Trans. Camb. Phil. Soc.,' vol. 21 (1907); Tschudi, 'Phys. Rev.,' vol. 18, 2nd Ser., p. 423 (1921).

‡ Hamburger, 'Tageblatt d. Nat. Ver. in Wiesbaden' (1887).



Figs. 1, 2, 2A.

It is almost identical with that used by Sears* and has proved a very convenient arrangement. A stout weight W, attached to a long brass rod which passes through a hole in the base of a wooden frame, is supported at C (fig. 2A), from a terminal F fixed in the frame, by a short length of 5 ampere fuse-wire. B is a gauge that can be clamped to the rod in any position and which is always brought flat up against the under-surface of the frame at the commencement of each experiment. This enables one to vary the withdrawal of the right hand rod at will, and ensures that during a complete series of observations the withdrawal remains constant. The dropping device is connected with the bar by a long piece of thread T which passes under a pulley A. An ebonite collar O prevents the thread from touching the bar during an experiment. By means of a light spring M, a fork D fastened to a metal plate L is made to press upon a crosspiece which is attached to the rod at C. The plate L and the terminal F are connected by thick leads through a rheostat and key to the alternating mains. The dropping device is supported at H from the arm of a strong stand, which is clamped to an independent table.

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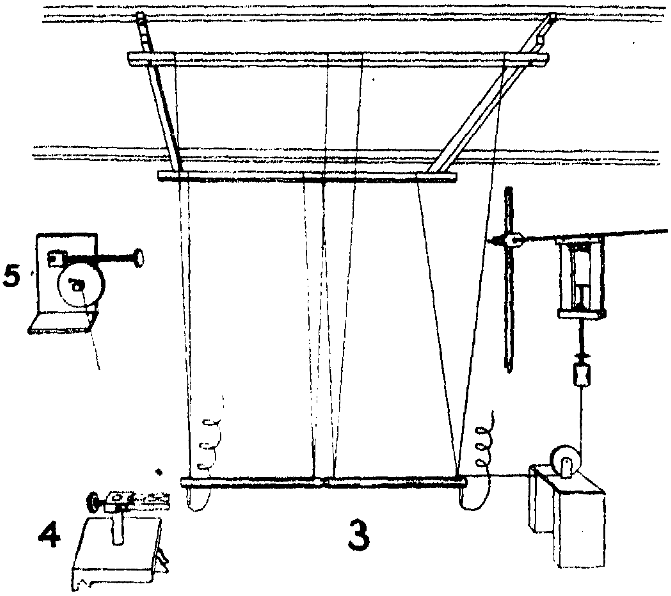
* J. E. Sears, 'Proc. Camb. Phil. Soc.,' vol. 14, pt. III (1908).



FIGS. 3, 4, 5.

Theory.

It is readily shown that the rate of discharge of a condenser of capacity C in a circuit of resistance R and self-inductance L is, for small values of L/R^2C, given by the formula

$$t = \frac{RC}{1+L/R^2C}\log_e\frac{q_0}{q_0-q}\,(1+L/R^2C),$$

where q_0 is the total quantity of electricity on the condenser initially, and q_0-q is the quantity remaining after time t. For two different values of R, say R_1 and R_2, we thus have on substitution and subtraction,

$$\frac{t}{C}\left(\frac{1+L/R_1^2C}{R_1}-\frac{1+L/R_2^2C}{R_2}\right)=\log_e\frac{q_0}{q_0-q_1}-\log_e\frac{q_0}{q_0-q_2}+\log_e\frac{1+L/R_1^2C}{1+L/R_2^2C}.$$

Curves have been plotted between $\log_{10}\frac{q_0}{q_0-q}$ and $1/R$ for different values of R;

for values of R not less than 500 ohms, they are found to be straight lines. Thus the term L/R^2C is negligible compared with unity within the limits of accuracy of the experiment. Moreover, the measurement of the slope of the line given by the ratio of $\log \frac{q_0}{q_0 - q_1} - \log \frac{q_0}{q_0 - q_2}$ to $1/R_1 - 1/R_2$ gives t/C where t is the time of impact. The graphical estimation of t has the further advantage that it provides a check on the observations, and a mistake in calculation is immediately noticeable. It is also to be noted that the lines do not go exactly through the origin of co-ordinates, so that estimations of t from a formula $t = RC \log_e \frac{\theta_0}{\theta_0 - \theta}$ are in error. This error is avoided in the graphical method.

Method of Experiment.

Initially the bars are adjusted so that when free and at rest they are just in contact. After suitably adjusting the position of the gauge B on the brass rod, the right-hand bar is withdrawn a measured distance (say 8 cm.). The condenser is charged up by inserting the plug P, and the galvanometer coil is reduced to rest by short circuiting it through its key. At a suitable instant, the fuse is fired, the key K (fig. 1) is released, thereby disconnecting the battery from the galvanometer, the bars impinge, the right-hand bar being reduced to rest and the left-hand one being picked up by the arrangement shown in fig. 4. A discharge q passes through the galvanometer and the throw θ of the latter is accurately noted. The total charge q_0 on the condenser is measured by observing the throw θ_0 when the bars are permanently in contact.

The first investigation with this apparatus was undertaken with a view to examining how the time of impact of two steel bars varies with the relative velocity of approach. The time of impact of two equal bars is measured for different withdrawals of the right-hand bar. This has been repeated for bars varying in length from 10 cm. to 60 cm. The time of impact is estimated by the equation

$$t = C \frac{\log_e \frac{\theta_0}{\theta_0 - \theta_1} - \log_e \frac{\theta_0}{\theta_0 - \theta_2}}{1/R_1 - 1/R_2} = 1 \cdot 6118 \tan \phi,$$

where ϕ is the slope of the line plotted through the observations. Also it is readily seen that, if T be the period of free swing of either of the rods and x the distance of withdrawal, the velocity at impact is given accurately by $v = 2\pi x/T$.

Table I.—Time of swing (T) of bars—2·428 sec.

Length of rods.	Velocity at impact. cm./sec.	$\log_{10} x$.	$t \times 10^4$ sec.	$\log_{10} (t \times 10^4)$.
10·5 cm.	5·564	0·3324	1·659	0·2199
	10·352	0·6021	1·455	0·1628
	15·528	0·778	1·351	0·1307
	20·704	0·903	1·242	0·0941
	25·880	1·000	1·186	0·0741
	31·056	1·079	1·148	0·0600
	41·408	1·204	1·045	0·0190
21·3 cm.	2·588	0·000	2·752	0·4396
	10·352	0·6021	2·031	0·3076
	15·528	0·778	1·881	0·2744
	20·704	0·903	1·780	0·2506
	25·88	1·000	1·685	0·2265
	31·056	1·079	1·608	0·2064
	41·408	1·204	1·537	0·1866
40·8 cm.	2·588	0·000	3·763	0·5756
	10·352	0·6021	2·940	0·4683
	15·528	0·778	2·713	0·4335
	20·704	0·903	2·592	0·4136
	25·88	1·000	2·473	0·3932
	31·056	1·079	2·383	0·3771
	41·408	1·204	2·289	0·3595
61·25 cm.	2·588	0·000	4·499	0·6531
	10·352	0·6021	3·629	0·5599
	15·528	0·778	3·440	0·5365
	20·704	0·903	3·278	0·5156
	25·88	1·000	3·141	0·4970
	31·056	1·079	3·058	0·4854
	41·408	1·204	2·943	0·4688

Corresponding values of $\log x$ and $\log (t \times 10^4)$ have been plotted for rods of lengths 10·5, 21·3, 40·8 and 61·25 cm.; and it appears from the straightness of the graphs that a simple relationship of the form $t = \mathrm{A}v^{\gamma}$ exists between v and t for each of the four lengths of bar used. The slope of the plot gives the value of γ, and it is seen to decrease slowly as l increases (fig. 6). In order to ascertain whether γ varies at all regularly with the lengths of the rods, l has been plotted against $-1/\gamma$ in fig. 7 (1). The broken line joining all the marked points is straight, indicating that for very short rods the time of impact varies inversely as $(\text{velocity})^{1/4 \cdot 1}$, and for very long rods the time of impact is independent of the velocity of approach. The interpretation for this latter case is, of course, that the time of impact is simply the time taken by the compressional wave started from the impact to travel once up and down the bars.

In general, we can assume the time of impact depends only on the length l of the bars, the density ρ of the material, Young's Modulus E for the bars, and the velocity v of approach at impact. The indices x, y, z can be chosen for a given value of γ so that t divided by $l^x\rho^yE^zv^\gamma$ is dimensionless, and, therefore, is a constant C. We thus obtain

$$[T]^1 = [L]^x \left[\frac{M}{L^3}\right]^y \left[\frac{MT^{-2}}{L}\right]^z \left[\frac{L}{T}\right]^\gamma,$$

subject to

$$1 = -2z - \gamma,$$
$$0 = x - 3y - z + \gamma,$$
$$0 = y + z,$$

so that

$$x = 1,$$
$$y = \frac{\gamma + 1}{2},$$
$$z = -\frac{\gamma + 1}{2},$$

giving

$$t = Clv^\gamma \left(\frac{\rho}{E}\right)^{\frac{\gamma+1}{2}}.$$

For long bars γ tends to zero; and we should have as above

$$t = 2l\Big/\sqrt{\frac{E}{\rho}}.$$

Thus C should be equal to 2.

For two spherical balls the theory of Hertz would require $\gamma = -1/5$. For short masses the form of the body, as well as its length would come into the formula; in the case of a sphere the form is expressed by the radius which takes the place of l, but the constant C has no longer the value 2.

For cylindrical bars, if t is plotted against the length l, the graph is not straight, so that t is not strictly a linear function of l. This fact is brought out in fig. 8, which shows t plotted against l for a velocity of approach equal to

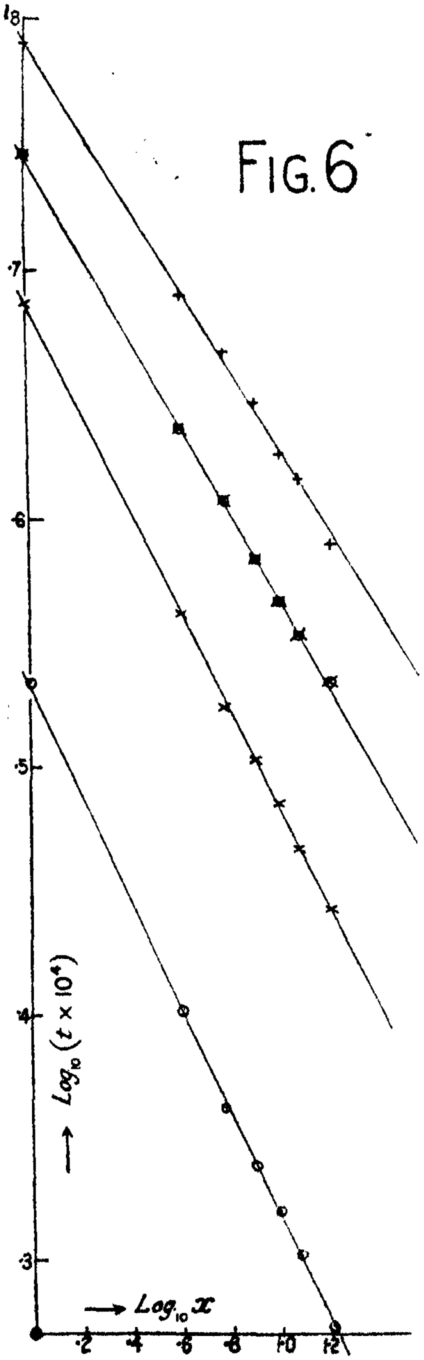


FIG. 6

2·6 cm./sec. Here our results differ slightly from those of Sears, who obtains a linear connection between l and t of the form

$$t = 2\,(l + b)\Big/\sqrt{\frac{\mathrm{E}}{\rho}},$$

where b would be an end-effect expressed by a slight addition to the length of the bar. This would probably be valid theoretically for bars moderately long compared with section, the value of b being proportional to the transverse

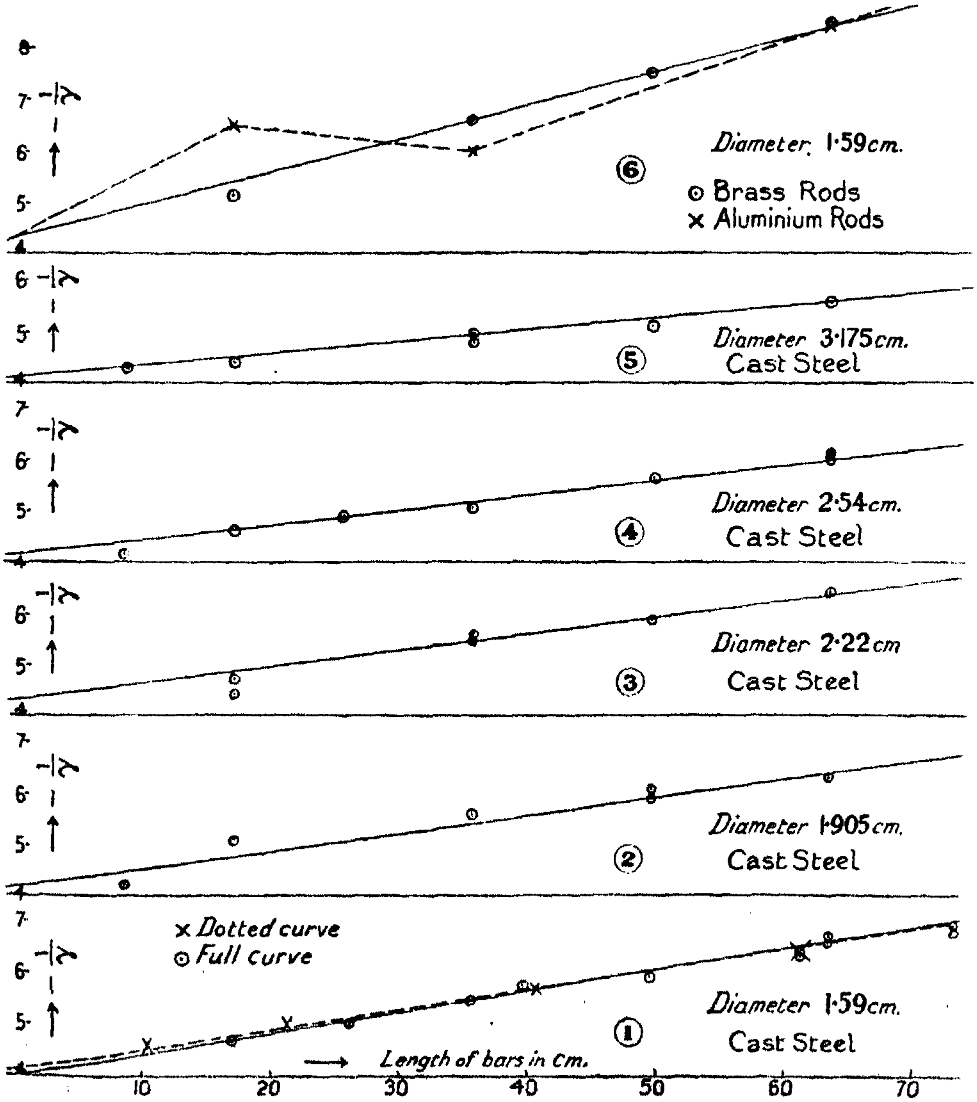


FIG. 7.

diameter. Inasmuch as he is able to deduce from his observations the velocity of sound along the rod, the result is in fact verified for his bars; but my observations do not maintain the linear relation between these two variables for shorter bars.

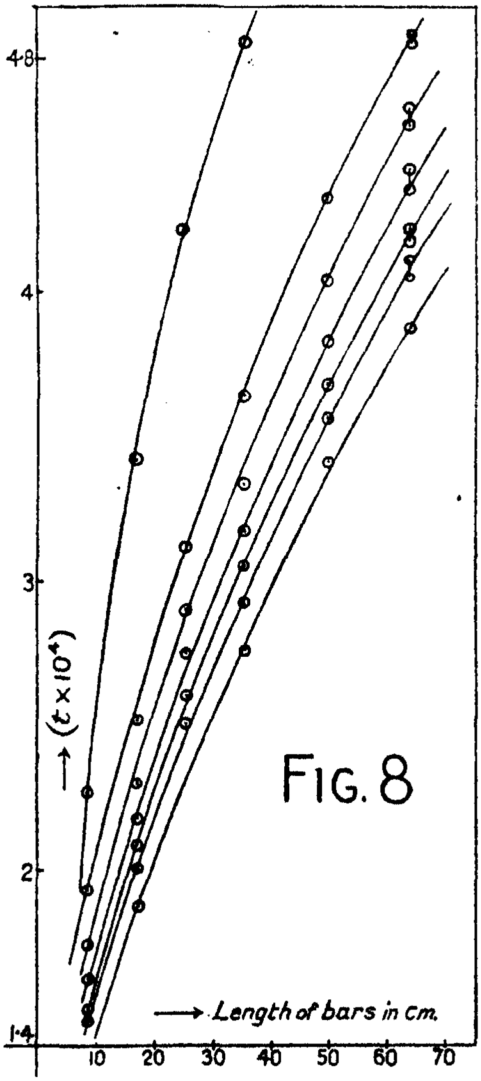


FIG. 8

Hitherto, only the variation of time of impact with velocity for particular pairs of bars has been considered. An attempt will now be made to combine these results so as to include bars of all lengths. Assume generally that the time of impact t is given by $t = v^{\gamma} f(l)$, where $f(l)$ is an unknown function of the length and includes any multiplying constants.

Since then $\log t = A' + \gamma \log x$, where A' is the intercept made by the line on the y axis (fig. 6), and $v = 2\pi x/T$, we obtain

$$\log f(l) = A' - \gamma \log 2\pi/T,$$

so that

$$f(l) = \exp(A' - \gamma \log 2\pi/T).$$

In the following table, the numerical values of $f(l)$ for all the lengths of bars used are tabulated, the quantity A' corresponding to the value of γ quoted in column 2 being measured from the appropriate curve. When $f(l)$ is plotted against l, the relationship is still non-linear. Further assume

$$f(l) = \left(\frac{83{\cdot}3\rho^{1/2}}{E^{1/2}}\right)^{\gamma+1} \phi(l),$$

as suggested by the formula, and obtain values of

$$f(l)\left(\frac{E^{1/2}}{83{\cdot}3\rho^{1/2}}\right)^{\gamma+1} = \exp(A' - \gamma \log 2\pi/T) \times \left(\frac{E^{1/2}}{83{\cdot}3\rho^{1/2}}\right)^{\gamma+1}.$$

Taking $(E/\rho)^{1/2}$ for the sample of cast steel used as 57×10^4 cm./sec., the following figures are then obtained :—

Table II.

Length of bars.	γ.	$1+\gamma$.	$t/v^{\gamma} = \exp(A' - \gamma \log 2\pi/T)$.	$\frac{t}{v^{\gamma}}\left(\frac{E^{1/2}}{83\cdot3\rho^{1/2}}\right)^{\gamma+1}$
10·5 cm.	$-\frac{1}{4\cdot6}$	$\frac{18}{23}$	$2{\cdot}417 \times 10^{-4}$	0·2325
21·3 cm.	$-\frac{1}{5}$	$\frac{4}{5}$	$3{\cdot}253 \times 10^{-4}$	0·3712
40·8 cm.	$-\frac{1}{5\cdot65}$	$\frac{93}{113}$	$4{\cdot}407 \times 10^{-4}$	0·6320
61·25 cm.	$-\frac{1}{6\cdot4}$	$\frac{27}{32}$	$5{\cdot}198 \times 10^{-4}$	0·9084

When columns 1 and 5 are plotted a linear relationship is sufficiently indicated. Thus

$$\phi(l) = A_1 + B_1 l = 0{\cdot}082 + 0{\cdot}01349\, l,$$

on measuring up the straight line through the points.

Thus

$$t = 0{\cdot}01349\,(l + 6{\cdot}07)\, v^{\gamma} \left(\frac{83{\cdot}3\rho^{1/2}}{E^{1/2}}\right)^{\gamma+1},$$

in which the addition to l again appears in the guise of an end-effect, gives the duration of impact for two steel bars of length l which approach one another with a relative velocity of v cm./sec. When various values are substituted in this formula, good agreement is obtained. This is shown in the following short table.

Table III.

Diameter cm.	Length of bars. cm.	Velocity of approach. cm./sec.	$t \times 10^4$. Experimental.	$t \times 10^4$. Calculated.
Series 1.				
1·59	10·5	5·564	1·659	1·590
	21·3	10·352	2·031	2·015
	40·8	25·88	2·473	2·475
	61·25	25·88	3·141	3·145
Series 2.				
1·59	16·95	15·7	1·646	1·632
	35·65	31·2	2·192	2·211
	49·6	10·42	3·199	3·234
	63·6	20·85	3·377	3·352

For long bars, the results again indicate that the time of impact is independent of the velocity of approach of the bars.

Thus when $l \rightarrow \propto, \quad \gamma \rightarrow 0$, and

$$t = (6 \cdot 83 + 1 \cdot 125\, l)\left(\frac{\rho}{E}\right)^{1/2}.$$

For very large values of l

$$t = 1 \cdot 125\, l\,(\rho/E)^{1/2}.$$

According to St. Venant, $t = 2l/V$ for very long rods, where V is the velocity of the compressional wave along the rod. For the very intense local stresses of impact, V may however be greater than $\sqrt{(E/\rho)}$, which is derived on the assumption of infinitesimal strain. On the other hand, exact quantitative results cannot be expected when extrapolating to lengths which are far outside the range of lengths used in the experiments. It is, however, clear that for these long bars, the impact is of the St. Venant type, being represented by a formula of the type $t = Cl/V$, where C lies between 1 and 2. The term 6·83 evidently depends on the rounded ends, and is in the nature of a small correction to compensate for the curvature of the ends.

In order to verify and extend the results so far obtained, more extensive series of observations are now begun. They include primarily observations on rods of cast steel of equal length, varying in diameter from 0·3176 cm. to 3·175 cm. and in length from 8½ cm. to 64 cm. The ends of the bars which come into contact are highly polished, and have a constant radius of curvature of 1·27 cm. as before. As it is desirable to preserve the same end conditions throughout a series, the shorter lengths are always obtained by cutting down the original bars in progressive stages. Before commencing the experiments, the bars are carefully aligned and adjusted so that the impinging bar is brought dead to rest by the impact. This is by far the most important adjustment to be made; for simple unloaded bars it is comparatively easy to arrange. It is impracticable to report details of the observations even in condensed form, as ten thousand independent readings have been taken during the course of the investigation. The accompanying table, however, summarises the main results as briefly as possible (see pp. 556–559).

In fig. 9, t is shown plotted, from these experiments, against l for different diameter bars, the velocity of the impinging bar being constant throughout and equal to 10·4 cm./sec. The time of impact does not appear as quite a linear function of the length; the departure from the linear form is greater for the thick than for the thin bars, as is to be expected, and the most striking feature is the important part thus played by the radius in modifying the time

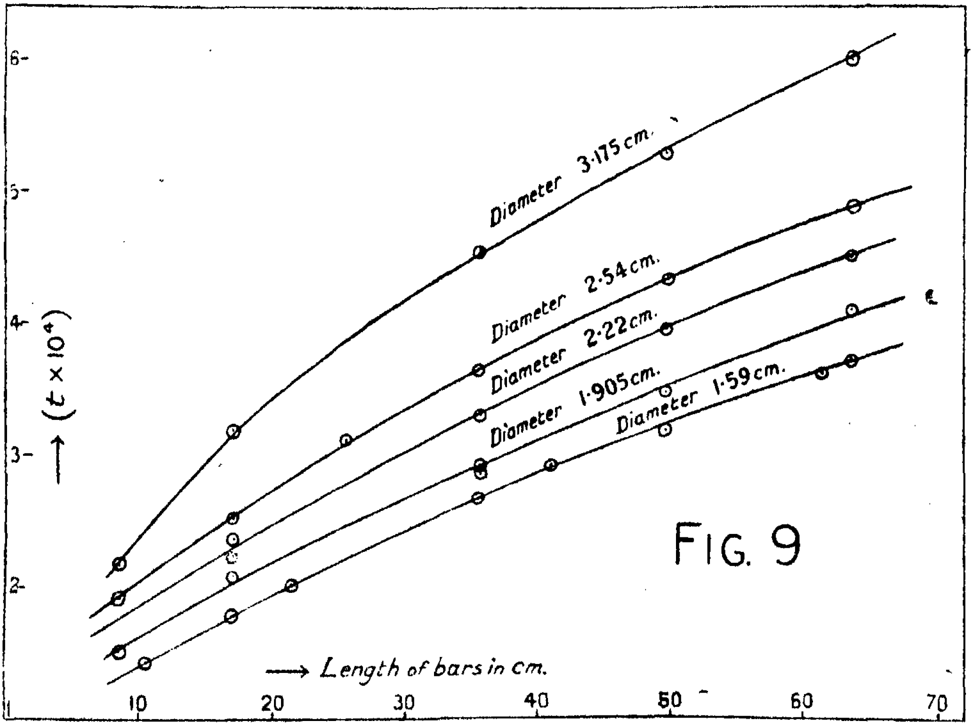


FIG. 9

Table IV.

Length of rods. cm.	Velocity at impact. cm./sec.	$\log_{10}$ ($t \times 10^4$).	Length of rods. cm.	Velocity at impact. cm./sec.	$\log_{10}$ ($t \times 10^4$).
Steel rods of diameter 1·59 *cm.*					
63·6	2·605	0·6813	63·6	2·607	0·6788
	10·42	0·5719		10·43	0·5744
T = 2·4115 sec.	15·63	0·5402	T = 2·41 sec.	15·64	0·5464
	20·84	0·5281		20·85	0·5285
	26·05	0·5105		26·07	0·5141
	31·25	0·4986		31·27	0·4933
	41·68	0·4843		41·71	0·4865
49·6	2·605	0·6084	35·65	2·601	0·5398
	10·42	0·5050		10·41	0·4288
T = 2·4115 sec.	15·63	0·4737	T = 2·4155 sec.	15·61	0·4002
	20·84	0·4563		20·81	0·3753
	26·05	0·4394		26·01	0·3579
	31·25	0·4247		31·20	0·3407
	41·68	0·4028		41·61	0·3217
16·95	2·619	0·3820			
	10·47	0·2548			
T = 2·4005 sec.	15·70	0·2166			
	20·94	0·1853			
	26·19	0·1684			
	31·42	0·1551			
	41·89	0·1268			
Steel bars of diameter 1·905 *cm.*					
63·6	2·594	0·7101	49·6	2·597	0·6410
	10·38	0·6128		10·39	0·5423
T = 2·422 sec.	15·56	0·5846	T = 2·4195 sec.	15·58	0·5132
	20·75	0·5648		20·77	0·4929
	25·94	0·5497		25·97	0·4736
	31·12	0·5441		31·16	0·4615
	41·50	0·5234		41·55	0·4499
35·6	2·599	0·5693	35·6	2·599	0·5834
	10·40	0·4573		10·40	0·4637
T = 2·418 sec.	15·59	0·4308	T = 2·418 sec.	15·59	0·4307
	20·79	0·4126		20·79	0·4098
	25·99	0·3936		25·99	0·3985
	31·18	0·3772		31·18	0·3868
	41·58	0·3620			
17	2·602	0·4506	8·5	2·599	0·3365
	10·41	0·3215		10·40	0·1844
T = 2·4145 sec.	15·61	0·2909	T = 2·418 sec.	15·59	0·1449
	20·82	0·2665		20·79	0·1064
	26·02	0·2465		25·99	0·0836
	31·22	0·2296		31·18	0·0757

Table IV—*continued.*

Length of rods. cm.	Velocity at impact. cm./sec.	$\log_{10}$ $(t \times 10^4)$.	Length of rods. cm.	Velocity at impact. cm./sec.	$\log_{10}$ $(t \times 10^4)$.
Steel bars of diameter 2·22 cm.					
63·6	2·604	0·7447	49·65	2·601	0·7032
	10·42	0·6552		10·40	0·5977
T = 2·413 sec.	15·63	0·6286	T = 2·416 sec.	15·60	0·5773 and 0·5725
	20·83	0·6120		20·80	0·5506
	26·04	0·5934		26·01	0·5337
	31·24	0·5816		31·20	0·5197
	41·66	0·5571		41·60	0·4872
35·6	2·600	0·6328	17	2·601	0·5167
	10·40	0·5207		10·40	0·3760
T = 2·417 sec.	15·60	0·4894	T = 2·4165 sec.	15·60	0·3336
	20·80	0·4652		20·80	0·3045
	26·00	0·4507		26·01	0·2808
	31·19	0·4368		31·20	0·2606
	41·59	0·4149		41·60	0·2421
17	2·602	0·4783	17		
	10·41	0·3516		31·21	0·2648
	15·61	0·3132			
T = 2·415 sec.	20·81	0·2894	T = 2·415 sec.	41·62	0·2370
	26·02	0·2661			
	31·21	0·2575			
	41·62	0·2354			
Steel bars of diameter 2·54 cm.					
	2·595	0·7901		2·595	0·7755
63·8	10·39	0·6887	63·8	10·39	0·6867
	15·57	0·6661		15·57	0·6604
T = 2·421 sec.	20·76	0·6458	T = 2·421 sec.	20·76	0·6386
	25·95	0·6251		25·95	0·6208
	31·13	0·6145		31·13	0·6080
	41·52	0·5885			
	2·600	0·7465		2·601	0·6868
49·8	10·40	0·6359	35·5	10·41	0·5615
	15·60	0·6068		15·61	0·5236
T = 2·417 sec.	20·80	0·5828	T = 2·4155 sec.	20·81	0·5019
	26·00	0·5660		26·01	0·4848
	31·19	0·5523		31·20	0·4665
	41·59	0·5337		41·61	0·4415
	2·594	0·6246		2·600	0·5345
25·5	10·38	0·4941	17	10·40	0·4022
	15·56	0·4631		15·60	0·3621
T = 2·4225 sec.	20·75	0·4396	T = 2·417 sec.	20·80	0·3387
	25·94	0·4162		26·00	0·3201
	31·12	0·3996		31·19	0·3025
				41·59	0·2736
	2·600	0·3572			
8·5	10·40	0·2867			
	15·60	0·2424			
T = 2·417 sec.	20·80	0·2125			
	26·00	0·1840			
	31·19	0·1709			

Table IV—*continued.*

Length of rods. cm.	Velocity at impact. cm./sec.	log$_{10}$ ($t \times 10^4$).	Length of rods. cm.	Velocity at impact. cm./sec.	log$_{10}$ ($t \times 10^4$).
Steel bars of diameter 3·175 *cm.*					
	2·594	0·8856		2·594	0·8885
63·6	10·38	0·7785	63·6	10·38	0·7805
	15·56	0·7465		15·56	0·7470
T = 2·422 sec.	20·75	0·7247	T = 2·422 sec.	20·75	0·7236
	25·94	0·7098		25·94	0·7064
	31·12	0·6922		31·12	0·6933
				41·50	0·6710
	2·596	0·8394		2·599	0·7720
49·6	10·39	0·7226	35·6	10·40	0·6554
	15·57	0·6902		15·59	0·6250
T = 2·42 sec.	20·77	0·6606	T = 2·418 sec.	20·79	0·5973
	25·96	0·6433		25·99	0·5771
	31·15	0·6301		31·18	0·5639
	41·54	0·6022		41·58	0·5412
	2·599	0·7850		2·597	0·6300
35·6	10·40	0·6577	17	10·39	0·5040
	15·59	0·6211		15·58	0·4685
T = 2·418 sec.	20·79	0·5994	T = 2·4195 sec.	20·79	0·4360
	25·99	0·5782		25·97	0·4130
	31·18	0·5610		31·16	0·3940
	41·58	0·5379		41·55	0·3681
	2·596	0·4888			
8·5	10·39	0·3390			
	15·57	0·3084			
T = 2·42 sec.	20·77	0·2796			
	25·96	0·2555			
	31·15	0·2406			
Steel bars originally of diameter 2·54 *cm. turned down to* 0·635 *cm.*					
	2·598	0·4957			
25·5	10·40	0·4142			
	15·58	0·3948			
T = 2·419 sec.	20·78	0·3813			
	25·98	0·3705			
	31·16	0·3650			
Steel bars of diameter 0·3176 *cm.*					
32·9	2·642	0·3796	32·85 32·9	2·629	0·1647
T = 2·378 sec.	15·85	0·3284		10·52	0·1080
	21·13	0·3189	T = 2·39 sec.	21·03	0·0806
Loaded with brass collars of mass 29·12 gm.	31·7	0·3134	Unloaded.	31·54	0·0638

Table IV—*continued.*

Length of rods. cm.	Velocity at impact. cm./sec.	$\log_{10}$ $(t \times 10^4)$.	Length of rods. cm.	Velocity at impact. cm./sec.	$\log_{10}$ $(t \times 10^4)$.
Brass rods of diameter 1·59 cm.					
63·6	2·592	0·7216	35·6	2·586	0·5442
	10·37	0·6380		10·35	0·4453
T = 2·424 sec.	15·55	0·6197	T = 2·43 sec.	15·51	0·4204
	20·73	0·6089		20·68	0·4015
	25·92	0·5986		25·86	0·3932
	31·10	0·5856		31·01	0·3848
	2·589	0·6614		2·593	0·3983
49·6	10·35	0·5594	17	10·38	0·2751
	15·52	0·5347		15·55	0·2485
T = 2·4275 sec.	20·70	0·5173	T = 2·423 sec.	20·74	0·2213
	25·89	0·5083		25·93	0·2003
	31·06	0·4954		31·11	0·1848
Aluminium bars of diameter 1·59 cm.					
	2·594	0·5323		2·592	0·4308
63·6	10·38	0·4675	35·6	10·37	0·3007
	20·75	0·4346		15·55	0·2602
T = 2·422 sec.	31·12	0·4112	T = 2·424 sec.	20·73	0·2331
				25·92	0·2109
				31·10	0·2027
	2·599	0·3896		2·592	0·1246
35·6	10·40	0·2886	17	10·37	0·0443
	15·59	0·2421		20·73	0·0003
T = 2·418 sec.	20·79	0·2349	T = 2·424 sec.	31·10	$\bar{1}\cdot9718$
	25·99	—			
	31·18	0·2031			
				31·10	$\bar{1}\cdot9750$
				10·37	0·0518
				20·73	0·0119
				31·10	$\bar{1}\cdot9870$

of collision. For 17 cm. bars, having a velocity of approach before impact of 15·63 cm./sec., $t_{3\cdot175\text{ cm.}}/t_{1\cdot59\text{ cm.}} = 1\cdot786$, and for 63·6 cm. bars under the same conditions, $t_{3\cdot175\text{ cm.}}/t_{1\cdot59\text{ cm.}} = 1\cdot585$, the ratio decreasing as the length increases. The way in which this circumstance is explained will be developed later.

From columns 2 and 3 of Table IV, curves have been constructed showing the relationships between times of impact and velocities of approach of the impinging bars at the instant of impact. For each series a simple equation of the form $t = Av^{\gamma}$ is revealed; and from the curve γ can be accurately calculated. In fig. 7, values of $-1/\gamma$ are shown plotted against l. For each size of bar $-1/\gamma$ is a linear function of l: moreover, the various lines for cast steel are nearly parallel. In passing from the 1·59 cm. to the 3·175 cm. bars, however, there is a slight change in the slope of the line; and this change is of theoretical interest as it affords strong evidence in favour of the hypotheses that have so far been made. This is brought out below where the values of A″ and B in the formula $-1/\gamma = A'' + Bl$ are tabulated.

Table V.

Metal.	Radius of bar. cm.	B.	$Br = K$.	A″.
Cast Steel.	0·1588	0·2021	0·03210	4·15
	0·7938	0·0412	0·03271	4·0
	0·9525	0·0348	0·03314	4·15
	1·1112	0·03226	0·03584	4·3
	1·27	0·02908	0·03693	4·15
	1·5875	0·02292	0·03639	4·12
Brass.	0·7938	0·06464	0·05123	4·3
Aluminium.	0·7938	0·06464	—	4·3

It is seen that while B decreases uniformly, the product Br is practically constant. A″ also changes only slightly. These results are necessary; for the exponent γ is a number and so of no dimensions, thus A″ is a constant and B is inversely proportional to r, the only other linear magnitude. The equation for γ thus becomes

$$-1/\gamma = A'' + Kl/r. \tag{I}$$

According to (I), an increase in $-1/\gamma$ can be produced as effectively by decreasing r as by increasing l. A critical method of testing the accuracy of a formula $1/\gamma = f(l/r)$ is thereby suggested. Two wire bars, 0·1588 cm. radius and 32·9 cm. long with well polished ends are made and suspended as before, and the times of impact for different velocities of approach measured. The results, included in Table IV, give $-1/\gamma = 10{\cdot}8$ as anticipated, and the product Br is the same as for bars 10 times as thick. As a confirmatory test, the times of impact of two bars 2·54 cm. diameter and 25·5 cm. long are found for different velocities of approach and γ deduced, giving $-1/\gamma = 4{\cdot}9$. On turning down the bars to 0·635 cm., leaving the ball ends and length untouched and repeating the experiments, $-1/\gamma$ is found to have increased to 9·1. This seems to afford sufficiently conclusive evidence that the formula $-1/\gamma = A'' + Kl/r$ represents the experimental results.

What is the significance of the two terms in equation (I)? In the bar problem, $1/A''$ is analogous to the index $\frac{1}{5}$ which Hertz derives from his statical theory of impact in the case of spheres. A″ is thus the statical factor in the impact and can be regarded as a dimensionless constant: when Kl/r is small $-1/\gamma = A''$, *i.e.*, the impact is determined completely by statical considerations. This happens when r/l is large, *i.e.*, for short stout bars or when K is small. In contradistinction to this, Kl/r can be regarded as the dynamic term, the quantity l/r being expressive of the way the geometry of the bar affects the problem. The quantity K which is independent of γ, r, l and v is thus independent of the geometry of the bars and the circumstances at the point of impact, and reflects something which happens later. It expresses to what extent the impact is governed by dynamic as distinct from static considerations. Since A'' is dimensionless, and γ, by its method of introduction into the problem is also dimensionless, K is dimensionless, although naturally it will be found later to vary for different metals. For long thin bars Kl/r is the predominating term and the impact is of the St. Venant type. Conversely when Kl/r is small, the impact is independent of the geometry of the bars, *i.e.*, it depends only on the curvature in the immediate neighbourhood of the point of impact and not on the shape or extent of the other parts of the body. On the other hand, when dynamic conditions prevail, the impact is not over until all

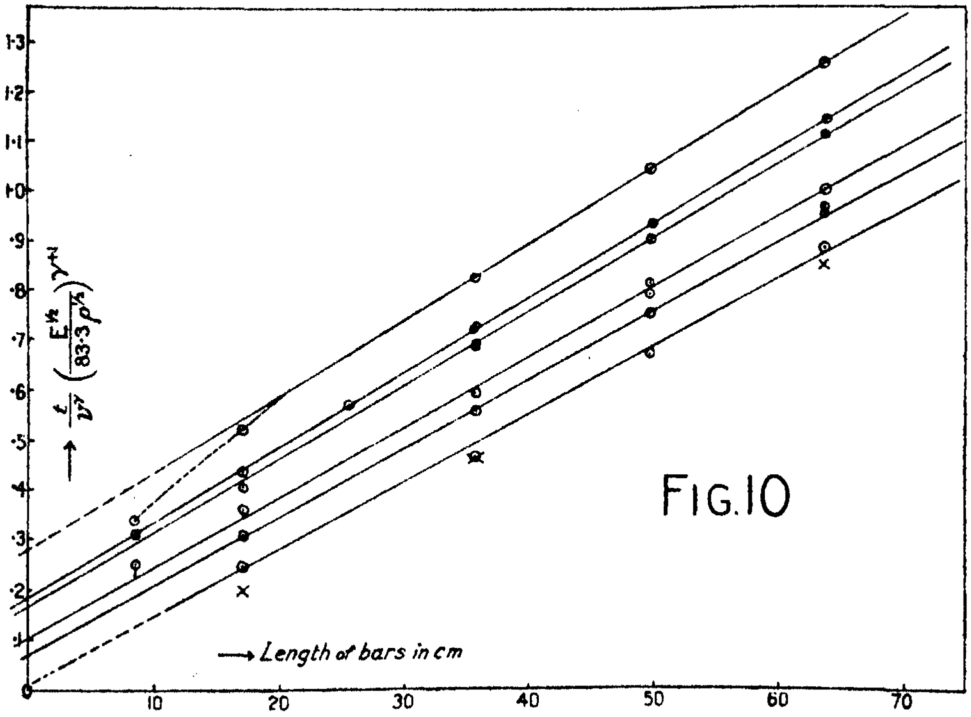


FIG. 10

Table VI.

Diameter. cm.	Length. cm.	γ.	$t/v^{\gamma} = \exp(A' - \gamma \log 2\pi/T)$.	$\frac{t}{v^{\gamma}}\left(\frac{E^{1/2}}{83\cdot 3\rho^{1/2}}\right)^{\gamma+1}$.	Slope of appropriate line in fig. 10.	Intercept on y axis. Experimental.	Intercept on y axis. Calculated.
1·59	63·6	−1/6·7	$5\cdot2972 \times 10^{-4}$	0·9703	0·013847	0·07	0·07
	63·6	−1/6·58	$5\cdot361 \times 10^{-4}$	0·9588			
	49·6	−1/5·93	$4\cdot750 \times 10^{-4}$	0·7553			
	35·65	−1/5·46	$4\cdot130 \times 10^{-4}$	0·5610			
	16·95	−1/4·68	$2\cdot96 \times 10^{-4}$	0·3070			
1·905	63·6	−1/6·32	$5\cdot936 \times 10^{-4}$	1·004	0·014155	0·10	0·10
	49·6	−1/5·9 −1/6·07	$5\cdot185 \times 10^{-4}$, $5\cdot121 \times 10^{-4}$	0·7943, 0·8179			
	35·6	−1/5·6	$4\cdot441 \times 10^{-4}$	0·5960			
	35·6	−1/5·63	$4\cdot441 \times 10^{-4}$	0·5960			
	17·0	−1/5·1	$3\cdot388 \times 10^{-4}$	0·3626			
	8·5	−1/4·2	$2\cdot629 \times 10^{-4}$	0·2496			
2·22	63·6	−1/6·42	$6\cdot533 \times 10^{-4}$	1·113	0·014855	0·16	0·14
	49·65	−1/5·87	$5\cdot941 \times 10^{-4}$	0·9034			
	35·6	−1/5·6	$5\cdot077 \times 10^{-4}$	0·6875			
	35·6	−1/5·5	$5\cdot116 \times 10^{-4}$	0·6927			
	17	−1/4·4	$3\cdot943 \times 10^{-4}$	0·4351			
	17	−1/4·7	$3\cdot665 \times 10^{-4}$	0·4046			
2·54	63·8	−1/6·07	$7\cdot232 \times 10^{-4}$	1·155	0·015149	0·18	0·18
				1·132			
	63·8	−1/6	$7\cdot211 \times 10^{-4}$	1·147			
	63·8	−1/6·1	$7\cdot127 \times 10^{-4}$	0·9371			
	49·8	−1/5·63, 1/5·58	$6\cdot572 \times 10^{-4}$, $6\cdot613 \times 10^{-4}$	0·9296			
	35·5	−1/5·05	$5\cdot7585 \times 10^{-4}$	0·7213			
	25·5	−1/4·9	$5\cdot076 \times 10^{-4}$	0·5729			
	17	−1/4·62	$4\cdot203 \times 10^{-4}$	0·4323			
	8·5	−1/4·17	$3\cdot343 \times 10^{-4}$	0·3088			
3·175	63·6	−1/5·57	$9\cdot135 \times 10^{-4}$	1·259	0·015414	0·28	0·28
	63·6	−1/5·57	$9\cdot164 \times 10^{-4}$	1·263			
	49·6	−1/5·1	$8\cdot309 \times 10^{-4}$	1·043			
	35·6	−1/4·98	$7\cdot283 \times 10^{-4}$	0·8461			
	35·6	−1/4·8	$7\cdot437 \times 10^{-4}$	0·8085			
	17	−1/4·4	$5\cdot409 \times 10^{-4}$	0·5200			
	8·5	−1/4·3	$3\cdot848 \times 10^{-4}$	0·3378			

			Brass rods.				
1·59	63·6	−1/8·5	$5·784 \times 10^{-4}$	0·8894	0·13662	0	0
	49·6	−1/7·5	$4·939 \times 10^{-4}$	0·6742			
	35·6	−1/6·6	$3·986 \times 10^{-4}$	0·4677			
	17	−1/5·15	$3·011 \times 10^{-4}$	0·2462			
			Aluminium rods.				
1·59	63·6	−1/8·4	$3·870 \times 10^{-4}$	0·8509	—	small	0
	35·6	−1/6	$2·833 \times 10^{-4}$	0·4636			
	17	−1/6·5	$1·638 \times 10^{-4}$	0·1969			
			Steel rods.				
0·3176 Loaded with brass collars of mass 29·12 gm.	32·9	−1/16·7	$2·520 \times 10^{-4}$	1·016			
0·3176 Unloaded.	32·9	−1/10·8	$1·596 \times 10^{-4}$	0·4821			
0·635 Turned down from 2·54 cm.	25·5	−1/9·1	$3·362 \times 10^{-4}$	0·8698			

the various parts of the system have been affected, and the time does depend on the shape and dimensions of the body.

In the extended series so far, the variation of t with v has been considered only for a particular pair of bars. An attempt will now be made to combine these results so as to include bars of all lengths and get a general expression for t. It can be assumed that $t = v^{\gamma}\left(\frac{83\cdot3\rho^{1/2}}{E^{1/2}}\right)^{\gamma+1}\phi(l)$, as suggested by the original dimensional equation, where 83·3 is a constant previously determined. If values of t/v^{γ} and $\frac{t}{v^{\gamma}}\left(\frac{E^{1/2}}{83\cdot3\rho^{1/2}}\right)^{\gamma+1} = \phi(l)$ are tabulated for the various lengths and diameters used (*v.* Table VI, columns 1, 2, 4 and 5), and if the values of l and $\phi(l)$ are plotted (*v.* fig. 10), it is seen that for each diameter of bar used, $\phi(l)$ is almost exactly a linear function of l, *i.e.*, $\phi(l) = A_1 + B_1 l$, where A_1 is the intercept made by the appropriate line on the y axis, and B_1 is the slope of the line. The quantity A_1/B_1, the end-correction to the length, must also have the dimensions of a length and be at the same time independent of l. It is here suggested that A_1 is of type Mr^2/a where r is the radius of the bar and a is the radius of curvature of the ball end.

The suggestion is completely substantiated by the results. In column 7, Table VI, the intercepts for the different diameters are tabulated, and almost complete agreement exists between the experimental values and the values calculated on the assumption that $A_1 = Mr^2/a$. It will be noticed at the same time that the bars of various diameters give lines which are practically parallel;

i.e.,
$$tE^{\gamma+1/2}/lv^{\gamma}\,83\cdot3^{\gamma+1}\,\rho^{\gamma+1/2}$$

is substantially independent of r, which verifies that by far the greater part of the variation of t with r occurs equally for all lengths of bars which are not too short. The slight variation with r, not accounted for by the additional term Mr^2/a, is due to the fact that accompanying every longitudinal propagation along the rod, there is a radial spread of the disturbance which becomes more important as the diameter of the rod increases. Such a subsidiary effect has clearly been neglected in the foregoing account: the problem has, however, been investigated by Pochhammer[*] who showed that as a result the velocity is reduced in accordance with an equation

$$V = V_0(1 - 4\pi\sigma^2r^2/\lambda^2),$$

where λ is the wave-length, and σ Poisson's ratio.

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[*] Pochhammer, 'Crelle,' vol. 81, 1876; or Love's 'Theory of Elasticity.'

The $8\frac{1}{2}$ cm. and 17 cm. readings for the 3·175 cm. bars lie below the positions they might be expected to occupy, and approach gradually the 2·54 cm. diameter readings. This is explained by the fact that owing to difficulties in grinding, the 3·175 cm. bars had to be coned down to 2·54 cm. diameter bars over a length of 4 cm. at the ball ends. This modification may produce quite considerable deviations for short lengths. For the various diameters used, the times of impact are thus given by the following simple equations.

Table VII.

Diameter. cm.	Time of impact.	Time of impact for long bars.
1·59	$t = (0 \cdot 1411\, r^2/a + 0 \cdot 013847\, l)\, v^{\gamma} \left(\frac{83 \cdot 3\rho^{1/2}}{E^{1/2}}\right)^{\gamma+1}$	$t = 1 \cdot 153\, l\, (\rho/E)^{1/2}$.
1·905	$t = (0 \cdot 1400\, r^2/a + 0 \cdot 014155\, l)\, v^{\gamma} \left(\frac{83 \cdot 3\rho^{1/2}}{E^{1/2}}\right)^{\gamma+1}$	$t = 1 \cdot 179\, l\, (\rho/E)^{1/2}$.
2·22	$t = (0 \cdot 1645\, r^2/a + 0 \cdot 014855\, l)\, v^{\gamma} \left(\frac{83 \cdot 3\rho^{1/2}}{E^{1/2}}\right)^{\gamma+1}$	$t = 1 \cdot 237\, l\, (\rho/E)^{1/2}$.
2·54	$t = (0 \cdot 1417\, r^2/a + 0 \cdot 015149\, l)\, v^{\gamma} \left(\frac{83 \cdot 3\rho^{1/2}}{E^{1/2}}\right)^{\gamma+1}$	$t = 1 \cdot 262\, l\, (\rho/E)^{1/2}$.
3·175	$t = (0 \cdot 1411\, r^2/a + 0 \cdot 015414\, l)\, v^{\gamma} \left(\frac{83 \cdot 3\rho^{1/2}}{E^{1/2}}\right)^{\gamma+1}$	$t = 1 \cdot 283\, l\, (\rho/E)^{1/2}$.

From column 3 it appears that for very long rods the time of impact is given by $Cl\, (\rho/E)^{1/2}$; the constant C comes out, however, definitely less than 2 and approximately 1·3. The most natural interpretation would seem to be that C remains equal to 2, but the wave, owing to its intense and adiabatic features, travels faster than the isothermal speed $(E/\rho)^{1/2}$.

An interesting confirmation of this result is obtained from a short series on steel bars of radius 0·1588 cm., where, as has been previously demonstrated, the effect over a short range of change of the initial velocity of approach on the duration of collision becomes negligible for comparatively short lengths.

Table VIII.—Steel bars of length 82·95 cm. and radius 0·1588 cm.

Velocity at impact. cm./sec.	$t \times 10^4$ sec.	γ.	$t = Cl\, (\rho/E)^{1/2}$.
15·85	2·130	−1/16·7	$1 \cdot 334\, l\, (\rho/E)^{1/2}$.
21·13	2·084		$1 \cdot 305\, l\, (\rho/E)^{1/2}$.
31·7	2·058		$1 \cdot 289\, l\, (\rho/E)^{1/2}$.

The times given in column 2 show only a 3 per cent. change corresponding to a 2 to 1 variation in the initial velocity of the impinging bodies. It is admissible therefore over the range chosen to write $t = Cl\,(\rho/E)^{1/2}$. This has been done in column 4 and C calculated. The mean value of C comes out at 1·3 ; so that the time of collision of two such bars is (for some reason) distinctly less than the time taken by the compressional wave started from the impact to travel once up and down the bars.

Finally, the expressions for t (column 3, Table VII) which are independent of the initial relative velocity of approach of the impinging bodies represent only limiting forms of the more general expressions in column 2, for values of l approaching infinity. Actually the effect of v is never entirely negligible whatever be the value of γ ; indeed for sufficiently small velocities the duration of impact can be extended indefinitely.

Brass and Aluminium Bars.

Complete series of observations are now taken with equal length bars of (*a*) brass ; (*b*) aluminium. The results with brass again indicate relationships of the form $t = \mathrm{A}v^{\gamma}$ and the values of $-1/\gamma$ for various values of l are plotted in fig. 7 (6). The points lie on a straight line ; but the slope of the line is 1·57 times greater than for steel bars of the same diameter. The aluminium rods proved very unsatisfactory and the values obtained for $-1/\gamma$ (indicated by crosses, fig. 7 (6)) are seen not to lie at all regularly on a curve. The inconsistences are undoubtedly due partly to the softness and lightness of the metal and also to the rapid oxidation of the polished ends which introduces unknown contact resistances. They do, however, indicate that the true curve is not very different from that for brass. The values of $\frac{t}{v^{\gamma}}\left(\frac{\mathrm{E}^{1/2}}{83{\cdot}3\rho^{1/2}}\right)^{\gamma+1}$ are given in column 5 of Table VI, and, as with steel, columns 1 and 5 are plotted in fig. 10. The best fitting straight line through the observation for brass (denoted by circles) is seen to be parallel to the corresponding lines for steel ; but the intercept on the y axis is extremely small. This indicates that the end correction $\mathrm{M}r^2/a$ in the expression $t = (\mathrm{M}r^2/a + \mathrm{B}_1 l)\, v^{\gamma}\left(\frac{83{\cdot}3\rho^{1/2}}{\mathrm{E}^{1/2}}\right)^{\gamma+1}$ is small, as if a tends to infinity. This is the case, of course, with these soft metals, as flats are developed at the point of impact whatever curvature is put on the ends initially. The quantity a is thus identified with the radius of curvature at the point of impact, the curvature of the surface at any other point being less important.

The values for aluminium, denoted by crosses, though much more uncertain thus generally confirm the conclusions drawn above.

Bars of Unequal Lengths and Loaded Bars.

The times of impact for bars of the same cross-section, of unequal lengths but equalised masses, and for loaded bars of equal lengths are next investigated. According to the dynamical theory, applicable to long bars of equal length, two such bodies should separate after an interval equal to the time taken by the wave to travel over twice the length of the longer bar, whatever be their relative masses.* According to the statical theory appropriate for short bodies, on the other hand, the time of collision is intimately associated with the masses of the bodies that collide; length no longer remains a direct factor in the impact. The smaller mass of the shorter bar can be compensated by attached loads.

The following experiments are intended to illustrate the ranges of application of the two theories. In all the experiments of this section, the pairs of bars are of the same diameter (1·59 cm.) and of identical weight, being equalised by providing the shorter bar with specially designed brass collars which grip the bar at eight points by thumb-screws. The procedure is exactly as before. In every experiment the shorter bar is made to impinge on the longer bar, and the durations of impact for various velocities of approach are found. In seven sets of readings the length of the impinging bar is 21·3 cm., while the longer bar varies in length from 26·15 cm. to 73·2 cm. A further set for bars of lengths 17 cm. and 73·2 cm. was performed, in order to see if any sudden discontinuity, such as may arise from harmonic sub-waves, occurs in the time for values of l greater than $4l_1$, where l and l_1 are the lengths of the two bars used.

In fig. 11, the results obtained are represented graphically: (1) and (2) show the results for a 73·2 cm. bar on which bars of length 21·3 cm. and 17 cm. impinge. For small velocities of approach, the points lie on a straight line, as with the simple bars, but for withdrawals in the neighbourhood of 8 cm., a discontinuity occurs and times begin to diminish very rapidly with further increase of velocity. The discontinuity is more marked, the greater the difference in length of the bars; compare (1) and (6). It is associated with a rapid decrease in the co-efficient of restitution of the bars. In (2′) the velocity of the impinging bar after impact is plotted against the corresponding velocity before impact. For withdrawals less than 8 cm. the velocity after impact is small, but for withdrawals exceeding 8 cm. a marked progressive increase in

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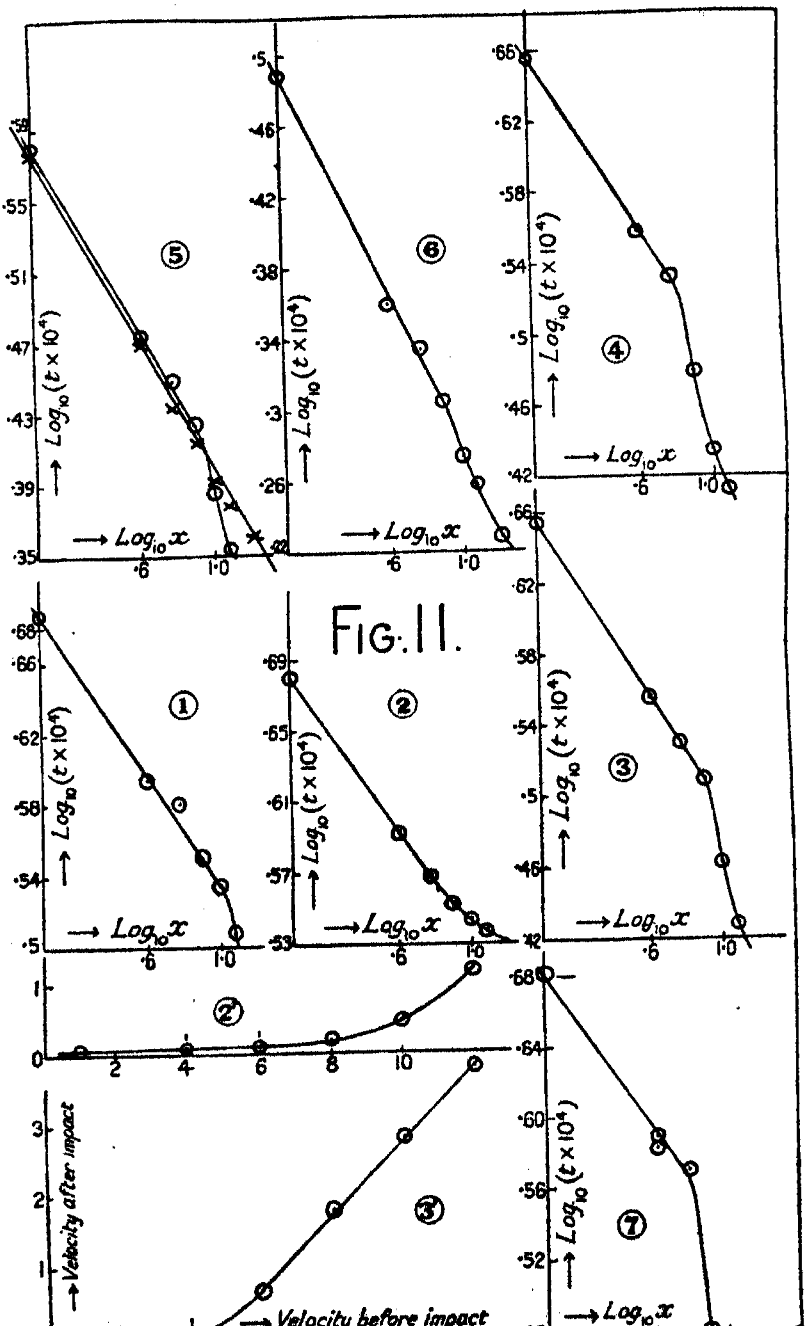
* St. Venant, 'Liouville's Journal,' vol. 12 (1867).


⑤
⑥
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⑦
→ $Log_{10}(t \times 10^4)$
→ $Log_{10}\,x$
→ Velocity after impact
→ Velocity before impact
·35
·39
·43
·47
·51
·55
·59
·5
·46
·42
·38
·34
·3
·26
·22
·66
·62
·58
·54
·46
·42
·68
·69
·65
·61
·57
·53
·64
·60
·56
·52
·48
·6
1·0
0
1
2
3
4
6
8
10
12

FIG. 11.

the ordinate appears. No such phenomenon occurs with simple bars for the same range of velocities. A necessary condition for a relationship of the form $t = Av^{\gamma}$ thus seems to be that the instant of greatest compression shall occur midway through the impact, and it breaks down for large values of v, because that hypothesis is no longer satisfied owing to the small values of e which enter. The same feature is exemplified in a striking manner in (3) and (3′), which refer to 21·3 cm. and 61·2 cm. bars.

The main points brought out by the curves of fig. 11 can be summarised thus:—

(i) For small and corresponding velocity of approach, the time of impact of two bars of the same cross-section of unequal lengths and equalised masses is identical with that for two equal bars of the same diameter as before, and of the length of the longer bar.

For instance (1) and (2) show practically the same times of impact although in (1) the impinging bar is 17 cm. long and in (2) 21·3 cm., while (3) and (4) give values of t the same as those obtained for two simple rods 61·2 cm. long.

(ii) The value of γ in $t = Av^{\gamma}$ corresponding to the straight portion of the curve, for two bars of the same diameter of unequal lengths but equalised masses, is identical with that obtained for two simple rods of the same diameter as before and of the length of the longer rod. The various values of $-1/\gamma$ are plotted in fig. 7 (1), and are seen to fit the line closely.

Is the impact then in these cases decided by the longer bar? To test this, two 17 cm. bars of cast steel (diameter 1·59 cm.) are loaded with brass collars to the weight of a 73·2 cm. bar of the same diameter (1·59 cm.), and the times of impact for different velocities of approach are measured. The results are shown in fig. 11 (7). For small velocities, the times are almost identical with those for two simple bars 73·2 cm. long, and γ is consequently practically identical in the two cases. A discontinuity occurs as before for withdrawals greater than 8 cm., owing to the asymmetric nature of the impact, and this becomes very pronounced at large velocities. Comparison figures for the same bars unloaded are given in Table IV.

In the case of equal bars of radius r, length l, and density ρ, each loaded with a mass M_0, a generalisation of equation (I) can be made for small velocities of approach. The relationship between duration of impact and velocity is still of the form $t = Av^{\gamma}$, where $-1/\gamma = A'' + K(l + l_1)/r$, l_1 being given by $\pi r^2 \rho l_1 = M_0$.

The cardinal point of interest in the case of loaded cylinders arises from the fact that when the circumstances are statical, so that the time of transmission of wave action is small compared with the time of impact, the results ought to depend only on the radii and materials of the surfaces that undergo direct impact, and on the masses of the bodies, but not on their form, except near the place of collision. The Hertz formula for equal spheres* can be put into the form

$$t = \frac{3 \cdot 294}{v^{1/5}} \left(\frac{m\,(1-\sigma)^2}{V^2 \rho r^{1/2}\,(1-2\sigma)} \right)^{2/5}, \tag{II}$$

where m is the mass, ρ the density, σ Poisson's ratio, r the radius of curvature at the surface of impact supposed spherical, V the velocity of sound, and v the initial relative velocity of the bodies in collision. In the following table, the times of impact derived from (II) are given along with the experimentally determined values, both for the loaded and the unloaded bars.

Table IX.

Velocity at impact, cm./sec.	t sec. Experimental.	t sec. Calculated from (II).
	Loaded bars.	
2·589	$4 \cdot 810 \times 10^{-4}$	$5 \cdot 326 \times 10^{-4}$
10·36	$3 \cdot 82 \times 10^{-4}$	$4 \cdot 035 \times 10^{-4}$
15·53	$3 \cdot 720 \times 10^{-4}$	$3 \cdot 722 \times 10^{-4}$
20·71	$3 \cdot 028 \times 10^{-4}$	$3 \cdot 514 \times 10^{-4}$
	Unloaded bars.	
10·36	$1 \cdot 863 \times 10^{-4}$	$2 \cdot 251 \times 10^{-4}$

The experimental values are in every case less than those derived from (II). In view of the foregoing results, exact quantitative agreement with (II) is not to be expected: but in a general way the impact of short bars is in accord with the principles laid down by Hertz in his statical theory.

In conclusion, it gives me the greatest pleasure to thank Professor Sir Joseph Larmor for the interest he has taken in the investigation, and for the many criticisms and illuminating suggestions he has offered me; and to thank also the Grants Committee of the Royal Society for defraying the cost of the apparatus.

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* Hertz, 'Crelle's Journal für Math.,' vol. 92 (1881); or 'Collected Papers.'

The Discontinuity of the Drying Process.

By E. A. Fisher, Department of Textile Industries, University of Leeds.

(Communicated by Prof. A. Smithells, F.R.S. Received 21 February, 1924.)

In three earlier papers* the results of a study of the rate of evaporation of water from wool, sand, kaolin, ball clay and various kinds of soil were described and discussed. The method of investigation consisted in exposing moist material over sulphuric acid in a closed vessel at a constant temperature, the apparatus being so constructed that the "drying" material could be weighed at frequent intervals without removing it from the drying vessel or in any way disturbing the drying conditions. In this way the percentage moisture content could be calculated each time the material was weighed, and curves were constructed by plotting on a large scale percentage water contents against time of drying. These experimental time curves were straight lines down to a certain critical moisture content which varied with different materials; below this point curvature commenced, slight at first but increasing later and diminishing again until the curve became almost straight at the extreme "dry" end of the curve. At the same time no sharp discontinuity could be detected by visual examination of the graphs. By measuring the tangents at different points along the curve values were obtained for the instantaneous rates of evaporation at different water contents under the particular drying conditions employed, and when the tangents were plotted against water contents (on a dry weight basis) the rate curves obtained, although of a relatively simple type, showed distinct and well marked discontinuities varying in number from two to four according to type of material dealt with. Each section of the rate curve was expressible by a simple type of equation. The factors determining the shape of the curves were discussed and this discussion was elaborated and extended in two subsequent papers.† The experimental side of this work is being rapidly developed and it is hoped that two further communications will be issued shortly that will carry the matter a stage further, while, at the same time, supporting in every way the conclusions already reached.

Recently, however, a paper has appeared in this Journal‡ by W. A. Davis

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* 'Roy. Soc. Proc.,' A, vol. 103, pp. 139, 664 (1923); 'J. Agric. Sci.,' vol. 13, p. 121 (1923).

† 'J. Agric. Sci.,' vol. 14 (1924).

‡ 'Roy. Soc. Proc.,' A, vol. 104, p. 512 (1923).

and J. V. Eyre entitled "The Discontinuity of the Hydration Process," in which some of the writer's main conclusions are controverted. These authors studied the "hydration" and "dehydration" of calcium sulphate and copper sulphate at two different humidities, and also flax fibres (natural, bleached and extracted), flax and ramie yarns and cotton wool, and found that "hydration" "took place in a series of discontinuous steps, the change in rate occurring at frequent intervals. Moreover, action was found to occur along a series of simple curves, generally either parabolic or linear . . . ." and each curve* consisted of a considerable number of segments, the discontinuities between which were sharp and visible on even casual visual inspection of small scale curves. All experimental and other details given in the paper relate to the "hydration" process only, and therefore do not necessarily have any bearing on the writer's work, but, without giving any details, Davis and Eyre state that precisely similar curves were obtained for the rate of "dehydration," or, as the writer prefers to call it, drying of these materials. This is definitely at variance with the writer's experimental results, and the authors say (p. 537) that "his (*i.e.*, the writer's) observations did not lead him to notice that the change is discontinuous, but he arrives at the conclusion that there is a change of rate by subjecting his curves to mathematical analysis. In this respect his conclusion is in agreement with ours, and his failure to obtain direct evidence may be attributed to the fact that his observations were not made at sufficiently frequent intervals."

The complete absence of details concerning the drying experiments in Davis and Eyre's paper is to be regretted, the more so as it makes criticism difficult, and it is to be hoped that such details will be published at an early date. Their statement, however, as to the writer's infrequent weighings, is untrue and is probably based on an examination of Table I in the writer's first paper, in which the time intervals between weighings were considerable and, in fact, unreasonably large. This table, corresponding to only nine experimental points in a moisture range of 46 per cent., was, however, given solely as "an example of the kind of data obtained" and the shortest table containing the largest time intervals was chosen for this purpose. The experimental curve given (Curve A, fig. 1) on the same page, shows 45 points (all that could be clearly shown on so small a scale) out of a total of 52 obtained in *six series of results*; the gaps left in one series were partially filled by results from other series. It is to be noted that the sextuplicate series agreed well with one another as also did quadruplicate* series on two and three thicknesses of the same material; such agreement would be surprising if such marked discontinuities as were observed by Davis and Eyre were really present in the drying process of the writer's materials under the experimental conditions employed. Davis and Eyre do not mention whether their curves represent each a single series of determinations on one sample of material or whether each curve is a mean curve of closely concordant replicate series: a close study of their paper rather suggests that the former is the case.

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* Corresponding to the writer's smooth experimental time curves.

The point at issue, however, is of such fundamental importance to the problem under investigation that closer examination of the available data seems to be called for, and in Table I are given the whole of the necessary data on which Curve A of fig. 1 of the writer's first paper was constructed and from which his main conclusions were drawn. The six series are combined into one table; the numbers in column 1 indicate the series to which the particular determination belongs so that any worker interested may be able to plot a curve for himself either for each individual series or for the whole six. Considerable care was exercised in cutting all samples exactly the same size, viz., 3½ inches by 2½ inches, so that the actual evaporating surface should be of the same shape and area in each case; owing to inequalities in thickness of the fabric (due to irregularities in the warp and weft yarns composing it) the dry weights were not identical in all cases. A correction therefore was made to the observed times to allow for this (except in series 1 and 2, in which the difference between the dry weights and their mean, which was taken as the "mean" for the six series, was only 0·15 per cent.) and these "corrected" times are given in column 3, and are those used in the construction of the curve. All the points obtained are given in the table—none have been omitted—and all lie on or very close to a smooth curve: the only bad point is the one marked † which, assuming the time as correct, lies about 0·45 per cent. below the curve; one other is 0·2 per cent. above the curve and a few more about 0·1 per cent. Some little irregularity would naturally be expected between replicate series of such material, especially in the regions where sudden changes in rate occur.

To test the matter further two fresh series of determinations have been carried out; one on the same heavily milled wool fabric (three thicknesses sewn together) previously dealt with and one on the same fabric unmilled or very lightly milled (two thicknesses). A lower temperature, a higher humidity and very frequent weighings were employed in order to eliminate any possibility of missing discontinuities that might be present. The temperature of the

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* Duplicate series were discussed in the first paper, others have been done since.

Table I.—Data for Drying of Wool Fabric (worsted warp and woollen weft). Single Thickness.

Series No.	Time (obs.).	*Time (cor.)	Water Content (percentage of dry weight).	Series No.	Time (obs.)	Time (cor.)	Water Content (percentage of dry weight).
	mins.	mins.			mins.	mins.	
2A	0·00	0·00	45·95	4A	90·25	87·50	5·95
3A	0·00	0·00	45·95	2	91·00	91·00	5·33†
1A	7·75	7·50	39·75	1A	95·25	92·00	5·90
4A	13·25	13·00	35·35	2A	115·50	112·25	4·38
1	15·00	15·00	34·27	1A	124·25	120·00	4·10
3A	17·50	17·50	32·10	1	125·50	125·50	3·79
2	18·50	18·50	31·21	2	129·00	129·00	3·72
3A	19·00	18·50	30·80	3A	148·00	146·50	3·13
4A	26·25	25·75	25·77	4A	156·25	151·50	2·87
1A	28·75	27·75	24·75	3A	192·00	190·25	2·30
1	32·00	32·00	22·33	2A	195·50	190·00	2·22
2	35·50	35·50	19·82	4A	200·25	194·25	2·06
3A	36·50	36·25	19·80	1A	203·75	195·53	2·10
1	43·50	43·50	16·10	1	207·50	207·50	1·92
4A	44·75	43·50	15·68	2	211·50	211·50	1·97
2	47·50	47·50	14·13	3A	246·00	243·50	1·54
2A	51·50	51·25	13·15	4A	254·25	246·75	1·51
1	58·00	58·00	10·90	2A	268·50	260·53	1·46
1A	61·75	59·75	10·75	1A	276·75	267·25	1·40
3A	64·00	63·50	9·79	3A	299·00	298·75	1·18
2	63·50	63·50	9·47	4A	306·25	297·25	1·16
2A	67·50	65·50	9·12	1	354·50	354·50	0·88
4A	72·25	69·25	8·12	2	358·50	358·50	0·98
1A	77·25	74·50	7·85	2A	384·5	373·00	0·86
3A	81·50	81·00	6·97	1A	393·75	380·00	0·85
2A	86·50	84·00	6·50				
1	86·50	86·50	6·23				

Mean weight of dry fabric = 1·929 gms.

Table II.—Results of Drying Wool Fabric (milled) over 55 per cent. Sulphuric Acid. (Three thicknesses sewn together.)

Time.	Water Content (percentage of dry weight).	Time.	Water Content (percentage of dry weight).	Time.	Water Content (percentage of dry weight).	Time.	Water Content (percentage of dry weight).
mins.		mins.		mins.		mins.	
0·00 (8·5° C.)	40·885	135·50	32·168	287·00	24·200	464·75	17·627
5·75	·485	141·25	31·719	292·50	23·939	470·75 (10·4°)	·452
10·00	·188	148·25	·418	297·25	·712	477·25	·278
15·75	39·788	153·25 (9·0°)	·139	303·25 (9·7° C.)	·450	483·75	·104
20·00	·492	161·00	30·721	308·25	·224	492·25	16·878
25·25	·143	165·25	·477	314·00	22·967	501·00 (10·5°)	·668
29·25	38·846	172·00 (9·1°)	·111	319·75	·700	506·25	·546
35·50	·445	176·25	29·849	325·75	·457	512·25	·407
39·75 (8·6° C.)	·183	182·75	·500	331·75	·195	518·75	·267
43·25	37·939	186·75	·291	337·75 (9·8°)	21·951	525·25	·128
47·50	·660	191·50	·029	346·00	·620	530·25	·005
51·75	·381	197·25 (9·2°)	28·716	356·75	·219	536·25	15·884
56·25	·085	202·00	·472	362·25	·010	541·25	·779
60·25	36·823	207·75	·158	371·00	20·661	549·00	·622
65·75	·492	212·50	27·914	377·5 (10·0°)	·434	555·25	·520
69·75	·231	218·75 (9·3° C.)	·583	382·75	·242	564·25	·326
73·00	·022	223·50	·321	389·50	·016	572·25 (10·6°)	·186
76·75	35·777	228·50	·024	394·25	19·876	579·25	·047
81·25	·498	234·50	26·763	399·00	·702		
88·25 (8·8° C.)	·045	240·00 (9·4°)	·531	404·50	·528		
94·75	34·644	245·50	·205	411·50 (10·2°)	·284		
100·75	·295	251·25	25·926	417·75	·074		
106·00	33·947	258·00	·595	425·00	18·848		
112·75	·563	263·75 (9·5°)	·316	432·75 (10·3°)	·586		
117·25 (8·9° C.)	·249	270·25	·002	439·50	·377		
124·25	32·900	275·25	24·758	446·00	·185		
120·75	·517	281·75 (9·6°)	·444	454·25	17·951		

Weight of dry fabric = 5·7355 gms.

Table III.—Results of Drying Wool Fabric (unmilled) over 55 per cent. Sulphuric Acid. (Two thicknesses sewn together.)

Time.	Water Content (percentage of dry weight).	Time.	Water Content (percentage of dry weight).	Time.	Water Content (percentage of dry weight).	Time.	Water Content (percentage of dry weight).
mins.		mins.		mins.		mins.	
0·00 (8·5° C.)	32·200	102·75	20·605	222·00 (9·3° C.)	14·174	356·00	11·593
8·75	30·930	109·00	·055	227·50	·005	365·00	·5085
13·00	·294	116·00	19·505	232·25	13·878	375·25	·424
19·75	29·448	121·00 (8·9° C.)	·125	238·00	·709	378·75 (10·0° C.)	·382
23·50	28·940	126·25	18·744	242·75 (9·4° C.)	·582	391·25	·297
28·75	·306	133·00	·278	248·50	·412	401·75	·212
33·25	27·755	139·00	17·897	254·00	·285	407·25	·170
37·50	·205	144·25	·560	261·00	·116	414·00 (10·2° C.)	·128
43·50 (8·6° C.)	26·486	150·00 (9·0° C.)	·220	266·50 (9·5° C.)	12·990	433·00 (10·3° C.)	·001
47·25	·063	156·50	16·840	272·50	·862	457·00	10·874
51·50	25·536	162·25	·540	278·00	·735	480·00 (10·4° C.)	·768
55·25	·133	169·00	·205	285·00 (9·6° C.)	·608	509·00 (10·5° C.)	·662
59·75	24·667	174·75 (9·1° C.)	15·951	289·50	·524	544·50	·577
64·50	·160	180·25	·697	295·00	·418	580·00 (10·6° C.)	·493
68·75	23·736	185·50	·486	306·00 (9·7° C.)	·228		
73·50	·228	190·75	·274	311·75	·142		
77·00	22·890	195·00	·105	317·00	·0585		
80·50	·551	200·50 (9·2° C.)	14·893	328·75	11·8895		
84·75	·170	205·25	·724	335·50	·805		
92·00 (8·8° C.)	21·536	210·00	·555	340·25 (9·8° C.)	·762		
98·00	20·986	216·50	·343	348·00	·678		

Weight of dry fabric = 2·3635 gms.

water bath rose slowly but steadily throughout the series from 8·5 deg. C. to 10·6 deg. C., the drying was carried out over 55 per cent. sulphuric acid corresponding to a relative humidity of about 30 per cent., and the weighings were performed every 3 or 4 minutes. In one case, 99 experimental points were obtained over a range of water content of 26 per cent., in the other 77 points were given over a range of 21 per cent. water content. The difference between adjacent points was never more than 0·5 or 0·6 per cent. water content (occasionally only at the extreme "wet" end of the curve) and was frequently as small as 0·05 per cent. or less (at the extreme "dry" end). The weighings were carried out continuously over a period of 11 hours.* The actual results are given in Tables II and III. The curve obtained on plotting the data given in Table II is fundamentally identical in type with that obtained from the earlier (replicate) series given in Table I, the irregularities being conspicuously fewer and smaller: only 1 point is as much as 0·1 per cent. water content off the curve and only 2 points are 0·05 per cent. away.

A careful examination of the large-scale curve obtained by plotting the data in Table III reveals the fact that although it is essentially similar in type to that obtained from Table II, in that no sharp discontinuities are present, the curve itself is not quite so "smooth" as is the latter: the curve appears very slightly flattened in places so that the curvature does not increase and decrease absolutely regularly from the "wet" to the "dry" ends of the curve: occasionally short regions, containing three or four points, could be represented almost as well by straight lines. *The irregularities are so slight that they would not appear at all if the curve were drawn on a small scale,* e.g., *that of the present page, and therefore bear no resemblance to the discontinuities noted by Davis and Eyre, which were altogether of a different order of magnitude.* These slight irregularities in curvature are of interest in another connection. Since the publication of the writer's earlier papers, fresh series have been carried out on the same fabric unmilled; with single thicknesses triplicate series were obtained comprising in all 26 experimental points over a range of water content of 47 per cent. and a time of drying of about 7 hours; and with two thicknesses sewn together sextuplicate series were plotted comprising 71 experimental points over a range of 51 per cent. water content and time of drying of rather less than 7 hours. The time intervals between weighings in any single series were unduly large so all the observations of the replicate series were combined into one series and plotted against time of drying. No curve at all could be drawn through the points: the points were scattered irregularly about a mean curve, the irregularity increasing progressively towards the "dry" end of the curve. The "agreement" was of the kind sometimes obtained in large-scale drying experiments on industrial plant, in which the drying conditions such as temperature, humidity and velocity of the air cannot be rigidly controlled.

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* **The writer's thanks are due to Mr. George Barker, M.Sc., for much help in carrying out these two series of determinations. Without Mr. Barker's assistance it would have been quite impracticable for a single worker to have carried out an uninterrupted series of weighings over so long a period.**

The difference between the good agreement between replicate series with the milled fabric and the disagreement between replicates with the same fabric unmilled is probably connected with structural differences between the two *fabrics*. A milled or felted woollen cloth may be compared with an engineering structure: during the process of milling the warp and weft threads and the wool fibres composing the threads, became "felted" or matted together. The actual nature of the felting action is not entirely understood, but the resulting material may be compared with a metal fabric in which the meshes are joined by welding: such a fabric cannot be unravelled without damaging the component threads and fibres, whereas an unmilled fabric can be unravelled without serious difficulty. A milled fabric therefore will offer considerable resistance to forces tending to displace threads and fibres from their relative positions, whereas unmilled fabrics, and, still more, cotton and linen fabrics and loose fibres and powders, will offer little resistance to such forces. In the drying of the latter kind of material any internal movements resulting in displacement of threads or fibres, even though too small to be visible, would certainly exert a disturbing effect on the rate of drying. It is conceivable that some such cause may account for the striking discontinuities observed by Davis and Eyre, and it would be of great interest if they could extend their work to felted wool fabrics or to agricultural or ceramic clays in which such internal movements are reduced to a minimum by "cohesion" of the fibres or particles.

It is significant that the only material examined by Davis and Eyre in which internal movements could be seriously restricted by rigidity of structure, viz., isinglass, showed none of the discontinuities noted with the other materials, although slighter irregularities of another type were exhibited in the earlier stages of the "hydration" process. That considerable internal movements of the type discussed do occur during drying is further suggested by a study of flax and kindred fibres carried out by C. R. Nodder* in Davis and Eyre's laboratory. Nodder showed that single flax and hemp fibres twist or untwist in a kind of spiral fashion during drying over a hot plate, and that they always untwist in opposite directions, so that the two kinds of fibres may be conveniently distinguished from each other in this way. Movements in twisted textile yarns on wetting have also been described by W. Harrison.[*] Moreover, forces adequate in magnitude for producing internal movements undoubtedly exist in a porous or capillary system of loose fibres or particles, in the considerable and varying tensions that small capillary water columns must be under when present in such systems as extremely small water wedges.[†]

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* 'J. Text. Inst. (Trans.),' vol. 13, p. 161 (1922).

Evidence of the possibility of such movements producing irregularities in drying curves has been obtained in the writer's laboratory in a somewhat different connection. A sample of alga (species of *Pleurococcus*) collected from a gate post was examined on account of its well-known ability to withstand without apparent injury long periods of drought.[‡] The alga was killed by prolonged desiccation over sulphuric acid and was then re-wetted and the rate of drying studied. During re-wetting water was rapidly absorbed and the mass swelled to several times its original apparent volume. During the later stages of drying the tensions on the capillary columns would provide conditions conducing to internal movements. The experimental time curve obtained was similar to the one obtained with the unmilled wool fabric, except that the flattened portions of the curve were longer and more pronounced, and an attempt to measure tangents to this curve graphically resulted in a rate curve of very ragged appearance. When the same (dried) sample was lightly ground and the whole of it passed through a sieve with 200 meshes per linear inch, no difficulty at all was experienced in obtaining a smooth drying curve, the rate curve also being smooth with no discontinuities and somewhat resembling the rate curve obtained for a gelatin gel discussed in an earlier paper.[§] Although considerable cracking occurred during the final stages of drying, the dried residue was a fairly coherent mass, the particles having stuck together during drying, behaving in this respect like clay. In some experiments on the drying of sodium phosphate—Na_2HPO_4, $12\,H_2O$—an extremely fine powder was obtained as a residue, which was by no means closely packed and which showed little tendency to "cake": here all the conditions are in favour of slight internal movements that would disturb the steadiness of the drying process and the experimental time curve obtained contained similar flattenings to those shown by the curves for unground alga and for unmilled wool fabric. *In no cases, however, have such large and striking discontinuities been noted as those observed by Davis and Eyre,* and while it is admitted that the intervals between the experimental points were unduly large with sodium phosphate and unground alga, this does not apply to the original experiments on milled fabrics nor to the two fresh series described above and detailed in Tables II and III on both milled and unmilled fabrics, nor does it apply to the observations recorded elsewhere on soils, clays and kaolin.

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[*] 'Roy. Soc. Proc.,' A, vol. 94, p. 460 (1918).

[†] Such tensions have been discussed in other connections by F. J. W. Whipple, 'Proc. Phys. Soc.,' Lond., vol. 34 (1922), Discussion on Hygrometry, p. 50; and by E. A. Fisher, 'J. Agric. Sci.,' vol. 14, p. 126 (1924); 'J. Phys. Chem.' (1924).

[‡] F. E. Fritsch, 'Ann. of Bot.,' vol. 36, p. 1 (1922).

[§] Full details will be given elsewhere at a later date ('J. Agric. Sci.').

The experimental results discussed above and in the writer's earlier papers, as well as in those of other investigators, indicate quite conclusively that the drying process is one of considerable complexity. The gross rate at which a system loses (or gains) water to (or from) the surrounding atmosphere depends on many factors, not all of which are constant throughout the whole process. The vapour pressure of the water in the system, the temperature, size and shape of the evaporating surface, the speed with which water moves from the interior of the system to the surface to replace water lost by evaporation, or from the interior to the surface of the individual fibres or particles, vary continuously as the drying proceeds and must exercise considerable influence in determining the rate of drying at different stages of the process : an attempt has been made in earlier papers to correlate changes in these factors with the shape of and discontinuities present in the rate of evaporation curves.

In view of these considerations, serious exception may be taken to the use by Davis and Eyre of the terms "hydration" and "dehydration" in this connection. Both hydration and dehydration are chemical changes, the mechanism in each case is a molecular one, and the rate at which such a change takes place can be accurately determined by appropriate experimental methods. As an example may be cited the measurement of the rate of hydration of fatty acid anhydrides in water by conductivity determinations. Davis and Eyre state (p. 522) that "it is clear that hydration in this case* is brought to rest, not as the result of a steady and continuously acting force, but by a series of abrupt changes in the molecular mechanism, as a result of which the velocity of change becomes smaller and smaller." They suggest here quite explicitly that they are measuring the rate at which the molecular process of hydration is taking place in this instance (and presumably with textile materials also). In point of fact, it is in the highest degree improbable that the rate of such a molecular process can be measured by the methods employed by Davis and

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* *i.e.*, absorption of water vapour by soluble anhydrite in air at 87 per cent. humidity.

Eyre and by the writer. What is being measured is the gross rate, expressed, *e.g.*, in grms. per unit time, at which a system loses (or gains) water to (or from) the surrounding atmosphere when the latter is maintained at constant temperature and humidity; or to express it somewhat differently, the rate measured is that of the slowest of a number of different processes taking place, simultaneously or consecutively, with different and varying velocities, and such that different processes become slowest of the series at different stages of the drying (or absorption) process.

The precise and accurate use of scientific terms is an obligation laid upon every scientific worker, and it is difficult to justify the application of such well understood terms as dehydration and hydration to such composite processes as drying and its opposite,* especially in view of the fact that the drying curves of the materials discussed above are essentially similar in type to that obtained with pure, extracted and ignited quartz sand, a substance that is not hydrated but merely wetted by water.

In one important respect only do the data given above in Table II differ from those in Table I and from those given in the earlier papers: curvature is present in all parts of the experimental time curve from 41 per cent. water content downwards. In the earlier work curvature began at about 31 per cent. water content, the graph for higher water contents being linear. A re-examination of the earlier data up to 125 per cent. water content with wool fabrics indicates that generally the time curve is straight down to a water content of about 31 per cent., but that occasionally, *i.e.*, with some samples, the experimental points are very irregularly placed between about 40 and 30 per cent. water content, and in these cases the points are always on the same side of the curve, suggesting that an irregular falling off in rate of evaporation occurs in this region. A similar irregularity has been observed occasionally with other materials. This portion of the curve is perhaps more liable to irregularities than any other, since the critical moisture content, *i.e.*, the moisture content at which the rate of evaporation begins to fall off from constancy, is in the narrow zone of water content in which the surface probably ceases to be completely covered with water, evaporation possibly falling mainly on the water wedges between the threads and fibres.† The equilibrium between the water and the rest of the system may be somewhat unstable in this region. The matter is being further investigated and is merely noted here.

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* Misuse of the term 'hydration' seems to be widespread. The writer has seen it applied to the imbibition of water by a gelatin gel immersed in water at a reaction removed from the iso-electric point, a phenomenon probably osmotic in origin and certainly not hydration in any 'chemical' sense of the term.

† *See* E. A. Fisher, 'J. Agric. Sci.,' vol. 14, p. 126 (1924).

Summary.

In previous papers a study has been made of the rates of drying of various colloidal materials of industrial interest, and it has been shown that, as a rule, very characteristic drying curves are obtained, which are essentially similar for all capillary systems both colloidal, *e.g.*, wool fabrics, clays, etc., and non-colloidal, *e.g.*, quartz sand.

Subsequently Davis and Eyre obtained drying curves for similar materials under not very dissimilar conditions that were entirely different in type from those obtained by the writer.

In this paper a detailed examination of the earlier data and of much fresh data is made, which entirely confirms the writer's earlier results and conclusions. Suggestions are made that may have bearing on the striking differences between the two sets of results.

On the Stability under Shearing Forces of a Flat Elastic Strip.

By R. V. Southwell and Sylvia W. Skan, of the Aerodynamics Department, National Physical Laboratory.

(Communicated by Prof. G. I. Taylor, F.R.S. Received January 21, 1924.)

Introduction and Summary. §§ 1–7.

1. This investigation relates to a flat elastic strip, of uniform breadth, thickness and material, upon which a uniform shear is imposed by tangential tractions applied at its edges and in its plane. The tractions appear in the expression for the change of potential energy which occurs when the strip is bent, and they must therefore affect both the modes and the frequencies of its free transverse vibrations. If sufficiently intense, they will bring about a condition of limiting elastic stability, since they can neutralize, in certain types of distortion, the restoring effects of the flexural stresses.

The results have some bearing on the stability of the webs of deep plate girders, which take the greater part of the total shear transmitted.* The correspondence must not, however, be pressed unduly, because in a girder uniform shear will be accompanied by a varying bending moment which imposes additional stresses upon the web. It is more accurate to describe the sheared strip (of which the length, in this paper, has been assumed to be infinite) as the limiting case either of a narrow annular disc,† or of a short tube,‡ subjected to torsion. The similarity of the three problems is illustrated by the specimens shown in fig. 1, which have buckled under conditions of limiting elastic stability.

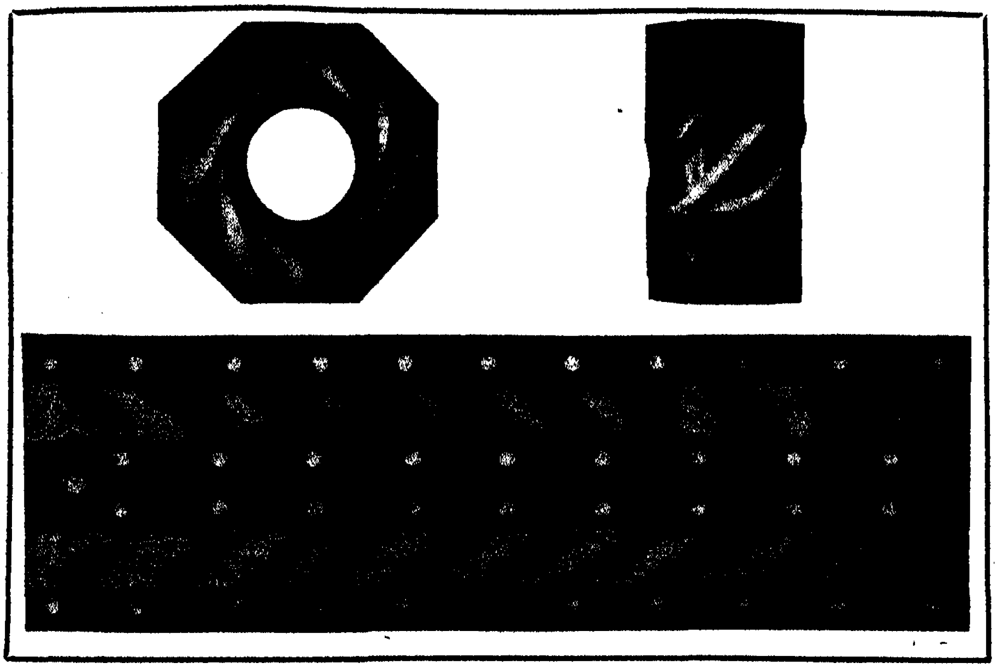

Fig. 1.

2. Calculations have been made under two different assumptions in regard to the constraints exerted upon the edges of the strip. In the first, transverse displacement is assumed to be prevented at the edges by transverse forces

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[*] Our problem has been studied experimentally, from this aspect, by W. E. Lilly; *cf.* 'Journal Junior Inst. Eng.,' vol. 18, pp. 72–81 (1907), and 'Engineering,' February 1, 1907.

[†] This problem has been investigated by Mr. W. R. Dean, in a paper which is to be published shortly.

[‡] Photographs illustrative of this problem have been published by W. E. Lilly in the first of the papers cited above.

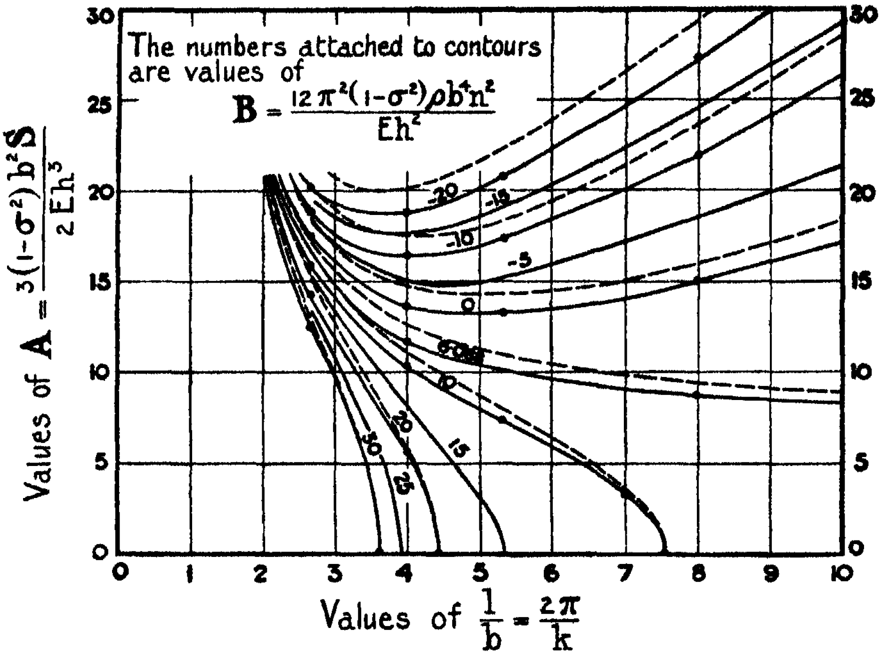

FIG. 2.—Variation of frequency with wave-length of distortion and with intensity of shear "Simply supported" edges: rotatory inertia neglected.

The following notation has been employed :—

$$\left.\begin{aligned}
\mathrm{S} &= \text{intensity of applied shearing forces, per unit length of edge.}\\
2b &= \text{breadth of strip.}\\
2h &= \text{thickness of strip.}\\
\rho &= \text{density of material.}\\
\mathrm{E} &= \text{Young's modulus for the material.}\\
\sigma &= \text{Poisson's ratio for the material.}\\
\mathrm{D} &= \text{“flexural rigidity” of strip} = \tfrac{2}{3}\,\mathrm{E}h^3/(1-\sigma^2).\\
w &= \text{transverse displacement of the middle surface of the strip.}\\
l = \frac{2\pi b}{k} &= \text{wave-length of the transverse displacement in a direction parallel to the edges.}\\
\mathrm{T} = \frac{1}{n} = \frac{2\pi}{p} &= \text{periodic time of the transverse vibration.}\\
\mathrm{A} &= \frac{b^2\mathrm{S}}{\mathrm{D}}.\\
\mathrm{B} &= \frac{2\rho h b^4 p^2}{\mathrm{D}} = \frac{12\pi^2(1-\sigma^2)\rho b^4 n^2}{\mathrm{E}h^2}.\\
\mathrm{C} &= \frac{h^2}{3b^2}.
\end{aligned}\right\}\quad (1)$$

only, no flexural couples being imposed; this is the condition known as "simple support." In the second, the slope of the middle surface of the strip, as well as its position, is fixed at the edges; this is the condition known as "clamping." The first problem attacked was the determination, for each of these conditions, of the frequency of transverse vibration in terms of the imposed shear. The results are presented, in non-dimensional form, in figs. 2 and 3.*

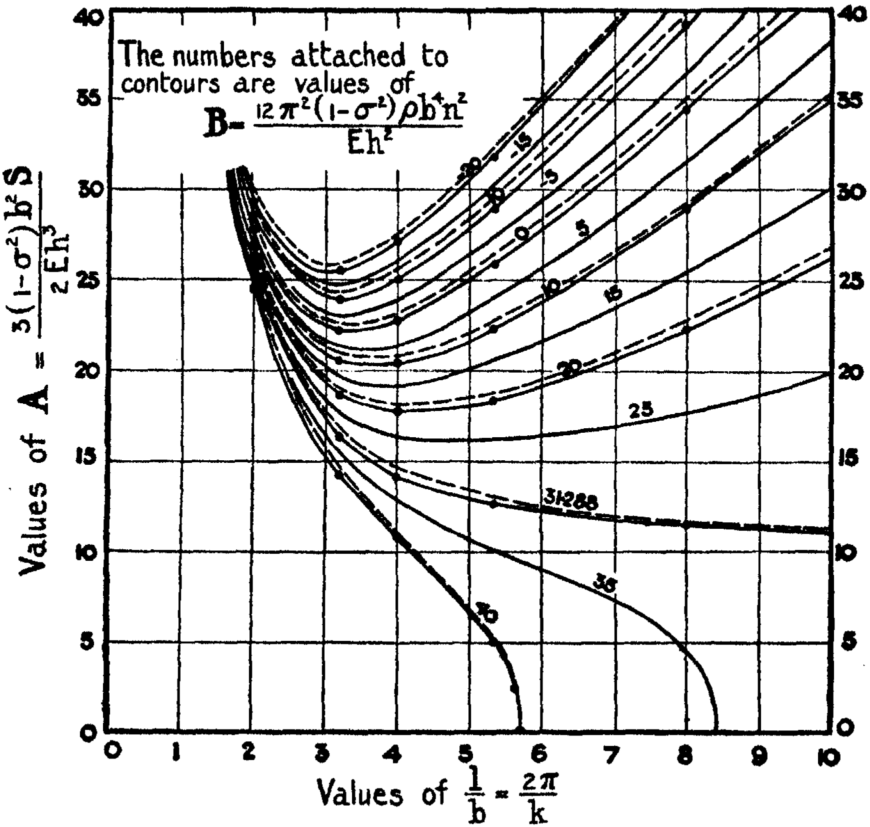

FIG. 3.—Variation of frequency with wave-length of distortion and with intensity of shear. "Clamped" edges: rotatory inertia neglected.

It will be seen that A is a non-dimensional quantity proportional to the intensity of shear, and B a non-dimensional quantity proportional to the square of the frequency of transverse vibration. In figs. 2 and 3 contours of constant B are plotted for a range of values of A and l/b. Since the length of the strip is infinite, no restriction is imposed upon the wave-length of the transverse displacement, and the diagrams show that, in consequence, the frequency of the vibrations associated with a given intensity of shearing force may have any value in excess of some definite minimum. The contours $\mathbf{B} = 6\cdot088$ for simply supported edges and $\mathbf{B} = 31\cdot288$ for clamped edges are asymptotic to the axis ($\mathbf{A} = 0$) in the direction $l/b \rightarrow \infty$; contours corresponding to higher values of **B** cut the axis ($\mathbf{A} = 0$) orthogonally,* whilst contours corresponding to lower values exhibit minimum values of **A**.

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* For the moment, regard should be paid only to the full lines. The significance of the dotted contours is explained in §4.

The plotted contours of **B** extend to negative as well as to positive values. The former relate, of course, to vibrations of imaginary frequency, *i.e.*, to continuously increasing (or decreasing) displacements, of an exponential type in respect of time, occurring under conditions of unstable equilibrium. Particular interest attaches to the contours which correspond to a zero value of **B**, and so relate to conditions of neutral stability: in these the minimum value of **A** has a special significance, since it is clear that "buckling" of the strip will occur in practice, if no steps are taken to prevent it, so soon as the shearing forces attain an intensity corresponding to this value; it is also clear that the resulting distortion will have a certain definite wave-length.

3. The minimum values of **A** for which the stability can become neutral are found to be $13\cdot21$ and $22\cdot18$ under the conditions of "simply supported" and of "clamped" edges respectively. It was to be expected that the first value would be lower. Taking representative figures for steel,† we deduce that a strip having a ratio of breadth to thickness of 100 : 1 would be liable to buckle under shear stresses of $6\cdot63$ and $11\cdot13$ tons per square inch respectively; these figures are well within the elastic limit of a high-grade steel, and should therefore be realized closely in experiment. The corresponding wave-lengths of transverse distortion are respectively $2\cdot67$ and $1\cdot6$ times the breadth of the strip.

For comparison with experimental results, the "mode" (or type) of the transverse displacement has been calculated under the limiting conditions which have just been considered. The results are exhibited in fig. 4, which shows contours of constant transverse displacement corresponding to the two types of edge-constraint; the numbers attached to the contours have a relative significance only, the absolute magnitude of the displacement being indeterminate. In both cases it is found, as was to be expected, that corrugations are formed in directions approximately perpendicular to the direction of maximum compressive stress; but the contours differ in certain minor features which have some theoretical interest.

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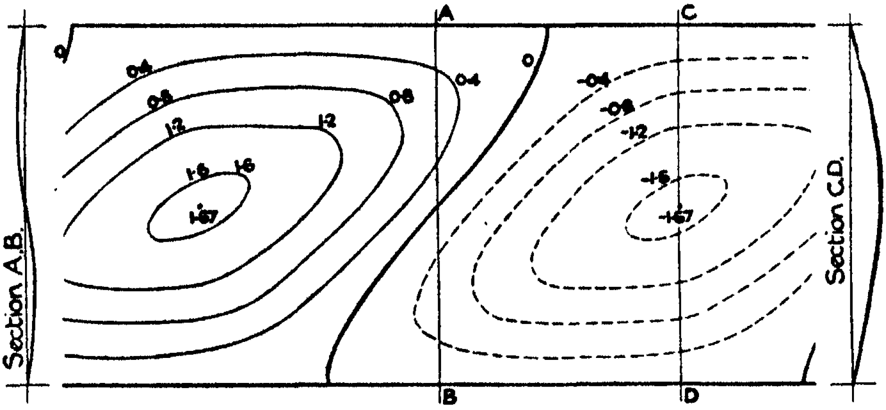
* *Cf.* §16 (March 12, 1924), pp. 598–9.

† $E = 13{,}700$ tons per square inch. $\sigma = 0\cdot3$.

4. The calculations involved in the determination of figs. 2 and 3 are of a "trial and error" type, leading to isolated solutions of the exact equations. From these isolated solutions (which are tabulated in Tables I and II) the corresponding contours can be derived by drawing smooth curves through the plotted points, and additional contours can then be obtained by cross-plotting; the contours for **B** = ± 5, ± 15, + 25, + 35 have been obtained in this way from the contours for **B** = 0, ± 10, ± 20, + 30, + 40.

"Simply supported" edges.



"Clamped" edges.

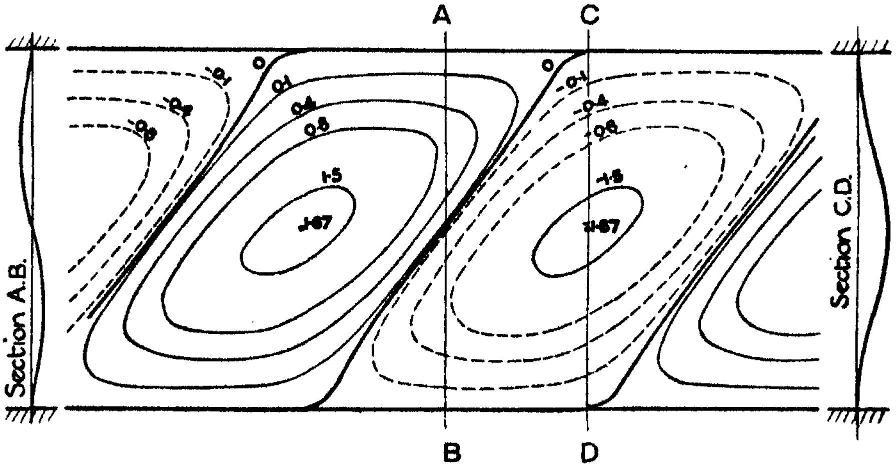


Fig. 4.—Distortion of strip under conditions of neutral stability.

Rotatory inertia has been neglected in these calculations, but methods are indicated* by which it can be taken into account, if such refinement is considered desirable; it has, of course, no effect upon the conditions of neutral elastic stability. As an alternative, an approximate treatment of the general equations is given, based on Lord Rayleigh's method of calculation from the energy condition for a displacement of an assumed type. It is known that the resulting estimate of frequency, if the type is suitably chosen, will approximate closely to the gravest frequency natural to the system under consideration, and that the error will be one of excess; hence, by including one or more arbitrary parameters in the expression for the assumed displacement, and choosing these in such a way as to make the resulting frequency a minimum, very close approximations can be obtained.† In the problem now under discussion considerable saving of labour can be effected by the use of these methods, and the accuracy attainable is indicated by the dotted contours of figs. 2 and 3, which relate to a strip in which rotatory inertia is neglected, and so compare with the accurate contours shown by full lines. Each dotted contour corresponds with the full-line contour lying next below it.

Methods are also indicated in the paper‡ whereby the fundamental solutions of figs. 2 and 3 may be used to obtain solutions for a strip which is subjected to uniform tension or compression (equal in all directions) in addition to the shear. The conditions of neutral stability can be determined very easily.

5. Mention should be made here of two important papers by G. H. Bryan relating to the stability of flat plating under edge thrusts acting in its plane.§ In the first paper, the forces considered are uniformly distributed thrusts acting in directions perpendicular to the edges, their intensities having any values T_1, T_2 for the two pairs of edges; in the second, the two thrusts are

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* See §18.

† *Cf.* H. Lamb and R. V. Southwell, on "The Vibrations of a Spinning Disc," 'Roy. Soc. Proc.,' A, vol. 99, pp. 272–280 (1921); and R. V. Southwell, "On the Free Transverse Vibrations of a Uniform Disc Clamped at its Centre, etc.," *ibid.*, vol. 101, pp. 133–153 (1922). The latter paper shows the importance of choosing a type of displacement which satisfies the boundary conditions completely.

‡ See § 19.

§ "On the Stability of a Plane Plate under Thrusts in its Own Plane, etc.," 'Lond. Math. Soc. Proc.,' vol. 22, pp. 54–67 (1891); and "On the Buckling and Wrinkling of Plating when Supported on Parallel Ribs or on a Rectangular Framework," *ibid.*, vol. 25, pp. 141–150 (1894). *Cf.* also A. E. H. Love, 'Mathematical Theory of Elasticity' (3rd Ed.), §332A. The case of a long strip subjected to edge thrust can be treated by exact methods, without recourse to the theory of flat plates; *cf.* R. V. Southwell, 'Phil. Trans. Roy. Soc.,' A, vol. 213, pp. 198–202 (1914).

combined with a uniform shear, the relative intensities of the three actions being such that they are the components of a simple thrust acting in some arbitrary direction. In both papers the discussion is extended to include rectangular plates of any finite length; but it is confined to the conditions of neutral stability, and the boundary conditions considered in the first paper are those of "simple support" alone, whilst in the second paper (which has the closer resemblance to the present investigation) the only condition which is imposed at the edges is that of zero transverse displacement, flexural couples as well as transverse forces being required in order to maintain the displacements considered.

Similar conditions at the boundaries have been assumed by S. Timoschenko, in a paper* dealing with several problems of elastic stability in flat plates, among which is included the case of a rectangular plate subjected to shearing forces. An approximate method of solution is here employed, generally similar to the method of Lord Rayleigh which has been described above.

6. As we have remarked already, our results have only a limited application to the practical design of girders, in which the conditions are more complicated than those considered in this paper. Some general conclusions may, however, be drawn. We have seen that it is necessary to contemplate the occurrence of elastic instability under stresses which the material could otherwise sustain without injury, and it has been shown that the wave-length of the distortion which is most likely to occur will depend upon the breadth of the strip, and not upon its thickness†: this result has an important bearing on the spacing of stiffeners in deep plate girders. The fact that the wave-length is roughly equal to the breadth of the strip indicates that satisfactorily comparable experiments could be made on fairly short specimens, and the results would have considerable theoretical interest, as examples of instability occurring under compound stresses.

7. On the practical side it is possible to go further. The design of light metal constructional members for aircraft is conditioned mainly by considerations of stability, and it is very important that their resistance to buckling should persist after the elastic limit of the material has been exceeded. The problems thus introduced are outside the present scope of analytical methods, but it is fairly clear that certain properties are desirable in the strip material used in

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* "Über die Stabilität versteifter Platten," 'Der Eisenbau,' vol. 12, pp. 147–163 (1921).

† A similar conclusion was drawn by W. E. Lilly from his experimental observations. *Cf.* 'Engineering,' *loc. cit.*, p. 137.

manufacture.* The need thus arises of some practical test which will serve to ensure that the material does in fact possess such properties, and it would seem that the most suitable test will be one in which a specimen cut from the strip is actually buckled under a measurable stress-system. It has been suggested that the stress-system considered in this paper would be convenient for the purpose, being easy to apply in practice to the strip material: by a suitable choice of distance between the clamped edges, the shearing stress required to produce instability could be raised to any required extent beyond the elastic limit of the material, and no delicate measurements would be required. Research in this direction is proceeding at the National Physical Laboratory, with the object of determining suitable dimensions, etc., for standardization as an acceptance test of the strip material.†

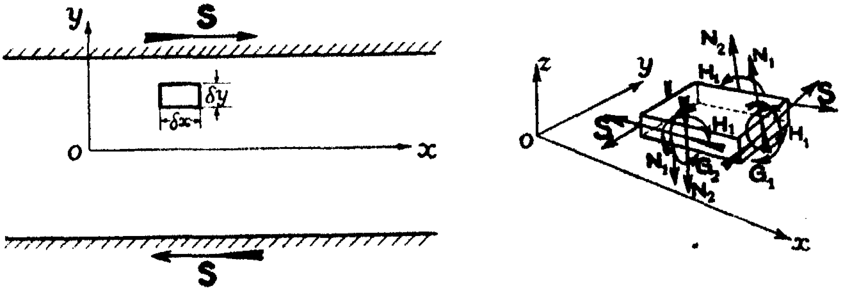

Fig. 5.

Our thanks are due to Miss V. M. Emms and to Miss M. P. Gurney, for assistance in the preparation of the illustrations to this paper, and to Mr. H. Gough, for the loan of specimens included in fig. 1.

8. *The Equation of Transverse Vibration.*—We shall employ the usual approxi-

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* Some discussion of the underlying physical principles involved was given in a paper cited above ('Phil. Trans.,' A, vol. 213, pp. 237–241).

† The strip included in fig. 1 is a specimen buckled in one of the preliminary tests. The symmetrical arrangement shown has been adopted for convenience in experiment: it was employed by E. G. Coker in his "Optical Determination of the Variation of Stress in a Thin Rectangular Plate subjected to Shear" ('Roy. Soc. Proc.,' A, vol. 86, pp. 291–319). Coker's experiments traced the effect of the free ends upon the distribution of shear in the plate—a problem which has also been investigated by E. N. da C. Andrade ('Roy. Soc. Proc.,' A, vol. 85, pp. 448–461). It would appear that the consequent modification of the buckling load, as compared with its theoretical value, will be small in comparison with the modification which results from the absence at the ends of resistance to transverse displacement, and the preliminary tests indicate that neither of the modifications is important in specimens of the dimensions shown in fig. 1.

mate theory of thin plates,* with rotatory inertia taken into consideration. Axes Ox, Oy (fig. 5) are taken in the middle surface of the undistorted strip, and the edges ($y = \pm b$) are assumed to be subjected to shearing forces, of uniform intensity S per unit length of edge, acting in the directions shown. The stress-resultants and stress-couples acting on a distorted element of the strip are exhibited on the right of fig. 5, and the equations governing the transverse displacement of the middle-surface are*

$$\left.\begin{aligned} \frac{\partial N_1}{\partial x} + \frac{\partial N_2}{\partial y} + 2S\frac{\partial^2 w}{\partial x \partial y} &= 2\rho h \frac{\partial^2 w}{\partial t^2}, \\ \frac{\partial G_1}{\partial x} - \frac{\partial H_1}{\partial y} - N_1 &= -\frac{2\rho h^3}{3}\frac{\partial^3 w}{\partial x \partial t^2}, \\ \frac{\partial H_1}{\partial x} - \frac{\partial G_2}{\partial y} + N_2 &= \frac{2\rho h^3}{3}\frac{\partial^3 w}{\partial y \partial t^2}. \end{aligned}\right\} \qquad (2)$$

Eliminating N_1 and N_2 from these equations, and substituting for G_1, G_2 and H_1 from the expressions*

$$\left.\begin{aligned} G_1 &= -D\left(\frac{\partial^2 w}{\partial x^2} + \sigma\frac{\partial^2 w}{\partial y^2}\right), \\ G_2 &= -D\left(\frac{\partial^2 w}{\partial y^2} + \sigma\frac{\partial^2 w}{\partial x^2}\right), \\ H_1 &= D(1-\sigma)\frac{\partial^2 w}{\partial x \partial y}, \end{aligned}\right\} \qquad (3)$$

we obtain as the differential equation to be satisfied by w

$$D\nabla_1^4 w - 2S\frac{\partial^2 w}{\partial x \partial y} + 2\rho h \frac{\partial^2}{\partial t^2}\left(w - \frac{h^2}{3}\nabla_1^2 w\right) = 0. \qquad (4)$$

∇_1^2 denotes the operator $\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2}$.

9. *Boundary Conditions.*—The boundary-conditions will relate to the constraints imposed along the edges $y = \pm b$. When these edges are simply supported, w and G_2 must vanish at all points on them; hence, and by (3), the conditions are

$$\left.\begin{aligned} &\left.\begin{aligned} w &= 0, \\ \frac{\partial^2 w}{\partial y^2} &= 0, \end{aligned}\right\} \text{when } y = \pm b. \\ &\text{When the edges are clamped, we have} \\ &\left.\begin{aligned} w &= 0, \\ \frac{\partial w}{\partial y} &= 0, \end{aligned}\right\} \text{when } y = \pm b. \end{aligned}\right\} \qquad (5)$$

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* *Cf.* Love, *op. cit.*, Chap. 22, from which the notation here employed for stress-resultants, etc., is taken. The remainder of the notation has been explained in equations (1) above.

The corresponding conditions which would hold at the other boundaries if the plate were of finite length are replaced in the case of the infinite strip by the single condition that w must be simply harmonic in x. The necessity for this condition may be seen if we regard the strip (as in §1) as the limiting case either of a short cylindrical shell or of a narrow annular disc, when the radius is infinite: it is clear that the wave-length of the transverse displacement in the direction of the x-axis will be unrestricted.

10. *Complex Periods Inadmissible.*—Our concern in this paper is with free vibrations in normal modes, for which the transverse displacement is harmonic in time, with real or imaginary period. By a known theorem,* it is unnecessary to contemplate the occurrence of complex periods (*i.e.*, periodic vibrations of increasing or decreasing amplitude) in systems of the type which we are considering. In the problem now under discussion, their impossibility may be very easily established as follows:—

Any solution of equation (4) in which $w \propto e^{ipt}$, where p is complex, may be written in the form

$$w_1 = (\mathrm{W} + i\mathrm{W}')e^{ip_1 t}, \tag{6}$$

where W and W′ are real functions of x and y. Then if

$$p_1{}^2 = \mathrm{P} + i\mathrm{Q}, \tag{7}$$

where P and Q are real constants, it is easily verified that the expression

$$w_2 = (\mathrm{W} - i\mathrm{W}')e^{ip_2 t}, \tag{8}$$

where

$$p_2{}^2 = \mathrm{P} - i\mathrm{Q}, \tag{9}$$

will also be a solution of equation (4).

Consider the integral

$$\frac{2\rho h}{\mathrm{D}}\iint (p_1{}^2 - p_2{}^2)\, w_1 w_2 \, dx\, dy, \tag{10}$$

in which the range of integration includes the whole area of the strip. In virtue of the differential equation (4), this integral is equivalent to the quantity

$$\iint (w_2 \nabla_1{}^4 w_1 - w_1 \nabla_1{}^4 w_2)\, dx\, dy + 2\frac{\mathrm{S}}{\mathrm{D}}\iint\left(w_1 \frac{\partial^2 w_2}{\partial x\, \partial y} - w_2 \frac{\partial^2 w_1}{\partial x\, \partial y}\right) dx\, dy$$

$$+ \frac{2\rho h^3}{3\mathrm{D}}\iint (p_1{}^2 w_2 \nabla_1{}^2 w_1 - p_2{}^2 w_1 \nabla_1{}^2 w_2)\, dx\, dy, \tag{11}$$

in which the range of the integrations is the same as before. But on transformation into line integrals, by Green's theorem, the first two integrals in (11) vanish, because at all points on the edges the quantities w_1, w_2, and one or other of the pairs $\frac{\partial w_1}{\partial y}$, $\frac{\partial w_2}{\partial y}$ and $\frac{\partial^2 w_1}{\partial y^2}$, $\frac{\partial^2 w_2}{\partial y^2}$ are zero, in virtue of the boundary conditions (5).

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* *Cf.* Whittaker, 'Analytical Dynamics' (2nd Ed.), §77; the outlines of an alternative proof are indicated in Lamb's 'Higher Mechanics,' §§ 92, 93. The special proof here given has been inserted for completeness, and in view of its relative simplicity.

The third integral in (11), on transformation by Green's theorem, becomes

$$-\frac{2\rho h^3}{3\mathrm{D}}(p_1{}^2 - p_2{}^2)\iint\left(\frac{\partial w_1}{\partial x}\frac{\partial w_2}{\partial x} + \frac{\partial w_1}{\partial y}\frac{\partial w_2}{\partial y}\right)dx\,dy,$$

and hence the identity of (10) and (11) gives the equation

$$(p_1{}^2 - p_2{}^2)\iint\left\{w_1 w_2 + \frac{h^2}{3}\left(\frac{\partial w_1}{\partial x}\frac{\partial w_2}{\partial x} + \frac{\partial w_1}{\partial y}\frac{\partial w_2}{\partial y}\right)\right\}dx\,dy = 0,$$

which, if we substitute from (6)—(9), takes the form

$$2i\mathrm{Q}\iint\left[(\mathrm{W}^2 + \mathrm{W}'^2) + \frac{h^2}{3}\left\{\left(\frac{\partial \mathrm{W}}{\partial x}\right)^2 + \left(\frac{\partial \mathrm{W}'}{\partial x}\right)^2 + \left(\frac{\partial \mathrm{W}}{\partial y}\right)^2 + \left(\frac{\partial \mathrm{W}'}{\partial y}\right)^2\right\}\right]dx\,dy = 0.$$

It follows, either that $\mathrm{W} = \mathrm{W}' = 0$ at every point in the strip, in which event the strip is not distorted, or that $\mathrm{Q} = 0$, so that complex periods do not occur.

11. *Equations in Non-Dimensional Form.*—It follows from the foregoing argument that we may assume a solution of the type

$$w = \mathrm{Y}e^{ikx/b}\sin p\,(t - t_0), \tag{12}$$

where Y is a function of y only, t_0 an arbitrary constant, and p^2 and k constants which are necessarily real. Then from (4) we have the equation

$$\left[\frac{d^2}{dz^2} - k^2\right]^2\mathrm{Y} - 2ik\mathbf{A}\frac{d\mathrm{Y}}{dz} - \mathbf{B}\left\{\mathrm{Y} - \mathbf{C}\left[\frac{d^2}{dz^2} - k^2\right]\mathrm{Y}\right\} = 0, \tag{13}$$

in which z is written for the ratio y/b, and the other symbols have the significance given in (1). All the quantities occurring in (13), with the exception of Y, are non-dimensional; neglect of rotatory inertia will involve the omission of the terms in C.

The corresponding forms of the boundary equations (5) are, for simply supported edges—

$$\mathrm{Y} = \frac{d^2\mathrm{Y}}{dz^2} = 0, \text{ when } z = \pm 1, \tag{14}$$

and for clamped edges—

$$\mathrm{Y} = \frac{d\mathrm{Y}}{dz} = 0, \text{ when } z = \pm 1. \tag{15}$$

12. *Solution of the Equations.*—If we now assume that

$$Y \propto e^{i\lambda z}, \tag{16}$$

we have from (13) the equation

$$\lambda^4 + (2k^2 - \mathrm{BC})\lambda^2 + 2\mathrm{A}k\lambda + k^4 - \mathrm{B}(1 + \mathrm{C}k^2) = 0, \tag{17}$$

which gives four values of λ corresponding to any one specified value for k. Denoting these four values by λ_1, λ_2, λ_3, λ_4, we may write

$$Y = \mathrm{P}e^{i\lambda_1 z} + \mathrm{Q}e^{i\lambda_2 z} + \mathrm{R}e^{i\lambda_3 z} + \mathrm{S}e^{i\lambda_4 z}, \tag{18}$$

where P, Q, R, S are undetermined coefficients. This expression may be substituted in the boundary conditions (14) or (15), and then, on eliminating P, Q, R, S, we obtain a determinantal equation which relates B with A and C.

The relation for simply supported edges may be thrown into the form

$$\begin{vmatrix} \sin\lambda_1, & \sin\lambda_2, & \sin\lambda_3, & \sin\lambda_4, \\ \cos\lambda_1, & \cos\lambda_2, & \cos\lambda_3, & \cos\lambda_4, \\ \lambda_1^2\sin\lambda_1, & \lambda_2^2\sin\lambda_2, & \lambda_3^2\sin\lambda_3, & \lambda_4^2\sin\lambda_4, \\ \lambda_1^2\cos\lambda_1, & \lambda_2^2\cos\lambda_2, & \lambda_3^2\cos\lambda_3, & \lambda_4^2\cos\lambda_4, \end{vmatrix} = 0,$$

which is equivalent to

$$\begin{aligned} &(\lambda_1^2 - \lambda_2^2)(\lambda_3^2 - \lambda_4^2)\sin(\lambda_1 - \lambda_3)\sin(\lambda_2 - \lambda_4) \\ &\qquad = (\lambda_1^2 - \lambda_3^2)(\lambda_2^2 - \lambda_4^2)\sin(\lambda_1 - \lambda_2)\sin(\lambda_3 - \lambda_4). \end{aligned} \tag{19}$$

For clamped edges the corresponding determinantal equation is

$$\begin{vmatrix} \sin\lambda_1, & \sin\lambda_2, & \sin\lambda_3, & \sin\lambda_4, \\ \cos\lambda_1, & \cos\lambda_2, & \cos\lambda_3, & \cos\lambda_4, \\ \lambda_1\sin\lambda_1, & \lambda_2\sin\lambda_2, & \lambda_3\sin\lambda_3, & \lambda_4\sin\lambda_4, \\ \lambda_1\cos\lambda_1, & \lambda_2\cos\lambda_2, & \lambda_3\cos\lambda_3, & \lambda_4\cos\lambda_4, \end{vmatrix} = 0,$$

which is equivalent to

$$\begin{aligned} &(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_4)\sin(\lambda_1 - \lambda_3)\sin(\lambda_2 - \lambda_4) \\ &\qquad = (\lambda_1 - \lambda_3)(\lambda_2 - \lambda_4)\sin(\lambda_1 - \lambda_2)\sin(\lambda_3 - \lambda_4). \end{aligned} \tag{20}$$

13. *Vibrations in an Unloaded Strip.*—Analysis very similar to the foregoing was employed in a paper "On the Stability of a Rotating Shaft, subjected simultaneously to End Thrust and Twist," which was published in the report for 1921 of the British Association Committee on Complex Stress Distributions in Engineering Materials*; the equation corresponding to (17), however,

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* *Cf.* British Association Reprint No. 4 (New Series), pp. 345–355.

contained a term involving λ^3 and no term involving λ. As in that paper, simpler methods can be employed when no odd term appears in the equation for λ. In the problem now under discussion, this happens when **A** (or **S**) is zero, so that equation (13) reduces to

$$\frac{d^4\mathrm{Y}}{dz^4}-(2k^2-\mathbf{BC})\frac{d^2\mathrm{Y}}{dz^2}+\{k^4-\mathbf{B}(1+\mathbf{C}k^2)\}\,\mathrm{Y}=0.$$

Comparing this equation with (14) of the earlier paper, we see that the results (18) and (19) of that paper can be applied directly if we substitute

$$-(2k^2-\mathbf{BC})\text{ for }\frac{\mathrm{P}l^2}{4\mathrm{EI}}\text{ (or B) of the earlier paper,}$$

and

$$-\{k^4-\mathbf{B}(1+\mathbf{C}k^2)\}\text{ for }\frac{\mathrm{W}\omega^2l^4}{16g\mathrm{EI}}\text{ (or C) of the earlier paper.}$$

We thus obtain, as frequency equations applicable to the unloaded strip: When the edges are simply supported (equation (18) of the earlier paper)—

$$\frac{4}{\pi^2}(2k^2-\mathbf{BC})+\frac{16}{\pi^4}\{k^4-\mathbf{B}(1+\mathbf{C}k^2)\}+1=0,$$

or

$$\mathbf{B}\left\{1+\mathbf{C}\left(k^2+\frac{\pi^2}{4}\right)\right\}=\left(k^2+\frac{\pi^2}{4}\right)^2; \tag{21}$$

and when the edges are clamped (equations (19) of the earlier paper)—

$$2(1-\cos\alpha\cosh\beta)=\frac{\alpha^2-\beta^2}{\alpha\beta}\sin\alpha\sinh\beta,$$

where

$$\left.\begin{aligned}\alpha^2&=2[\sqrt{4\mathbf{B}+\mathbf{B}^2\mathbf{C}^2}-(2k^2-\mathbf{BC})],\\ \beta^2&=2[\sqrt{4\mathbf{B}+\mathbf{B}^2\mathbf{C}^2}+(2k^2-\mathbf{BC})].\end{aligned}\right\} \tag{22}$$

14. *Inadmissibility of Certain Apparent Solutions.*—As in the earlier paper, it can be shown that certain relations which would apparently lead to simple solutions of the general equations (19) or (20) are in fact inadmissible. For example, the relation (19) could be satisfied by writing

$$-\lambda_2=\lambda_1=\frac{n\pi}{2},$$

where n is integral; but since the equation (17) contains no term in λ^3, the sum of its roots must be zero, and hence, if any two roots were equal in magnitude and opposite in sign, the coefficient of λ would also vanish, and the applied shear would be zero. This is the limiting case just treated.

Again, the coefficient of λ^2 in (17) is necessarily positive, since if BC were greater than k^2 we should have, from (1),

$$\frac{b^2p^2}{k^2} > \mathrm{E}/(1-\sigma^2)\,\rho,$$

and the vibration could be resolved into two distortion patterns advancing in opposite directions along the strip with a speed (pb/k) greater than the velocity of sound.* Hence, by "Descartes' Rule of Signs," equation (17) cannot have more than two real roots, and solutions of the type represented by

$$\sin(\lambda_1 - \lambda_2) = \sin(\lambda_1 - \lambda_3) = 0$$

are inadmissible.

Finally, although the equations (19) and (20) would both be satisfied if equation (17) had equal roots, solutions for the general case cannot be obtained in this way. If we merely substitute λ_1 for λ_2 (say) in the expression (18), we shall reduce the effective number of the arbitrary constants from four to three, and it can be shown that the boundary conditions will not then be satisfied unless Y is zero for all values of z. If, on the other hand, we write down the complete solution (with four arbitrary constants) under the condition of equal roots, we are in effect substituting λ_1 for λ_2 in an expression for Y which differs from (18) in having $e^{i\lambda_2 z}$ replaced by $ze^{i\lambda_2 z}$; but after this modification is made in (18), and the frequency equations obtained by the same methods as before, they are found to be no longer satisfied identically when λ_2 is made equal to λ_1.

It thus appears that the criteria (19) and (20) do not admit of simplification, and must be solved as they stand.

15. *Solution of the Frequency Equations* (19) *and* (20).—Since the coefficients in equation (17) are all real, imaginary or complex roots will occur in pairs. Moreover, as we have seen already, the sum of λ_1, λ_2, λ_3, λ_4 is zero. We may therefore write

$$\left.\begin{aligned} \lambda_1,\ \lambda_2 &= \alpha \pm \beta, \\ \lambda_3,\ \lambda_4 &= -\alpha \pm \gamma, \end{aligned}\right\} \qquad (23)$$

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* The velocity with which waves of extension are propagated along the strip (assuming lateral contraction to be prevented in the direction of its breadth, but to occur freely in the direction of its thickness) is $\sqrt{\mathrm{E}/(1-\sigma^2)\rho}$. *Cf.* §18.

where α is necessarily real, and β and γ either real or pure imaginaries. Then by comparing coefficients we find that

$$\left.\begin{aligned} -2\alpha^2-\beta^2-\gamma^2 &= 2k^2-\mathbf{BC}, \\ -\alpha(\beta^2-\gamma^2) &= \mathbf{A}k, \\ (\alpha^2-\beta^2)(\alpha^2-\gamma^2) &= k^4-\mathbf{B}(1+\mathbf{C}k^2), \end{aligned}\right\} \qquad (24)$$

where **A**, **B** and **C** have the values given in (1).

Substituting from (23) in (19) and (20), we obtain the equations

$$8\alpha^2\beta\gamma[\cos 2\beta\cos 2\gamma-\cos 4\alpha] \\ =[4\alpha^2(\beta^2+\gamma^2)-(\beta^2-\gamma^2)^2]\sin 2\beta\sin 2\gamma \qquad (25)$$

and

$$2\beta\gamma[\cos 2\beta\cos 2\gamma-\cos 4\alpha]=[4\alpha^2-\beta^2-\gamma^2]\sin 2\beta\sin 2\gamma, \qquad (26)$$

as frequency relations corresponding to the conditions of simply supported edges, and of clamped edges, respectively.* Our problem is thus reduced to that of satisfying (25) or (26) by values of α, β and γ which are related with the data of the problem by the three equations (24).

Solutions can be obtained by a process of trial and error. We have seen that α must be real, and it is evident from (24) that its sign merely affects the sign of **A** (*i.e.*, of **S**). To find the value of **A** corresponding to any specified real values of k, **B** and **C**, we may therefore assume some real negative value for α, and derive corresponding values for $(\beta^2+\gamma^2)$ and $(\beta^2-\gamma^2)$ from the first and third of (24). We thus obtain simultaneous values for α, β and γ which may be substituted in both sides of the frequency relation (25) or (26). The relation will not in general be satisfied; but the ratio of the expressions on the left and right hand sides may be plotted against the assumed value of α, and in this way, by trial, simultaneous values of α, β and γ can be found which make the ratio unity, and so constitute a solution. Inserting these in the second of equations (24), we obtain the value of **A** which corresponds to the specified values of k, **B** and **C**.

16. *Results for a Strip having Negligible Rotatory Inertia.*—When **C** is zero (*i.e.*, if rotatory inertia is neglected) the results can be plotted in the form of curves relating **A** and k for different constant values of **B**. By means of (1) these may be interpreted as relating the applied shear **S** and the wave-length l of the transverse displacement, for different constant values of the frequency n.

Figs. 2 and 3 exhibit the results for simply supported and for clamped edges respectively, and Tables I and II summarize the calculations upon which they are based. The labour of calculation is of course considerable, since each point in the final curves has to be derived by cross-plotting from a series of trials; but progress becomes more rapid when the general trend of the curves is known.

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* *Cf.* equations (45) and (47) of the paper cited in §13.

Table I.—Solutions for Strip with Simply Supported Edges. Rotatory Inertia Neglected.

B.	$2\pi/k$.	α.	β.	γ.	**A.**
30	2	−2·039	1·483	5·500i	21·07
	2·67	−1·483	1·469	4·202i	12·48
	3·62	0	1·571	2·913i	0*
20	2	−2·098	1·481	5·544i	22·00
	2·67	−1·626	1·461	4·304i	14·25
	4	−0·825	1·482	2·914i	5·62
	4·44	0	1·571	2·545i	0*
10	2	−2·153	1·480	5·586i	22·89
	2·67	−1·747	1·457	4·397i	15·91
	4	−1·309	1·427	3·225i	10·37
	5·33	−0·992	1·423	2·602i	7·40
	7	−0·480	1·508	2·085i	3·54
	7·55	0	1·571	1·964i	0*
6·088	2	−2·172	1·479	5·600i	23·20
	4	−1·418	1·418	3·312i	11·73
	8	−0·986	1·383	2·256i	8·79

B.	$2\pi/k$.	α.	β.	γ.	**A.**
−20	2	−2·300	1·475	5·700i	25·39
	2·67	−2·022	1·448	4·624i	20·14
	4	−1·864	1·405	3·723i	18·79
	5·33	−1·838	1·377	3·381i	20·80
	8	−1·837	1·352	3·132i	27·22
−10	2	−2·254	1·477	5·664i	24·60
	2·67	−1·941	1·451	4·554i	18·83
	4	−1·730	1·406	3·592i	16·38
	5·33	−1·676	1·377	3·208i	17·35
	8	−1·656	1·349	2·922i	21·87
0	1	−3·840	1·520	10·523i	69·20
	1·33	−2·996	1·505	8·039i	42·56
	2	−2·205	1·479	5·626i	23·77
	2·67	−1·850	1·452	4·479i	17·42
	4	−1·556	1·410	3·430i	13·63
	5·33	−1·445	1·383	2·977i	13·21
	8	−1·366	1·350	2·605i	14·97
0 (2nd Solutions)	1	−4·454	3·048	11·310i	97·27
	1·33	−3·772	3·019	9·054i	72·91
	2	−3·236	2·974	7·038i	60·12
	2·67	−3·056	2·948	6·203i	61·23
	4	−2·942	2·915	5·545i	73·55
	5·33	−2·911	2·902	5·305i	90·33
	8	−2·893	2·889	5·130i	127·70

* Calculated from equation (21).

The contours **B** = 6·088 for simply supported edges and **B** = 31·288 for clamped edges are asymptotic to the axis (**A** = 0); these values of **B** have been determined from the simplified criteria (21) and (22) by making k zero. The same equations have been employed for the determination of points in which the axis (**A** = 0) is cut by the contours for higher values of **B**. [These contours must cut the axis orthogonally; for it will be evident from an inspection of equations (24) — (26) that to every solution defined by values α, β, γ, **A**, **B**, **C**, k there will correspond another solution defined by $-\alpha$, β, γ, $-$ **A**, **B**, **C**, k, and hence, that if the curves of figs. 2 and 3 were extended to include negative values of **A** they would exhibit symmetry with respect to the axis ($\mathbf{A} = 0$).]* The contours for $\mathbf{B} = 0, \pm 10, \pm 20, +30, +40$, and also the asymptotic contours, have been drawn through points obtained by calculation, and the contours for $\mathbf{B} = \pm 5, \pm 15, +25, +35$ have been derived from them by interpolation.

Table II.—Solutions for Strip with Clamped Edges. Rotatory Inertia Neglected.

B.	$2\pi/k$.	α.	β.	γ.	**A.**
40	2	−2·166	1·769	5·679*i*	24·41
	3·2	−1·458	1·884	3·939*i*	14·17
	4	−1·110	1·983	3·366*i*	10·78
	5·33	−0·471	2·197	2·837*i*	5·15
	5·65	−0·220	2·249	2·762*i*	2·51
	5·75	0	2·265	2·742*i*	0*
31·288	3·2	−1·607	1·858	4·041*i*	16·18
	4	−1·382	1·915	3·524*i*	14·16
	5·33	−1·118	2·008	3·051*i*	12·67
	8	−0·775	2·152	2·658*i*	11·54
20	2	−2·266	1·762	5·755*i*	26·13
	3·2	−1·763	1·832	4·157*i*	18·54
	4	−1·620	1·865	3·697*i*	17·68
	5·33	−1·494	1·900	3·293*i*	18·35
	8	−1·390	1·937	2·975*i*	22·31
10	2	−2·311	1·756	5·788*i*	26·91
	3·2	−1·878	1·816	4·250*i*	20·43
	4	−1·775	1·836	3·822*i*	20·32
	5·33	−1·701	1·854	3·464*i*	22·27
	8	−1·658	1·868	3·197*i*	28·96
−20	5	−2·439	1·750	5·891*i*	29·32
	3·2	−2·143	1·783	4·480*i*	25·41
	4	−2·103	1·790	4·121*i*	27·07
	5·33	−2·089	1·793	3·836*i*	31·83
	8	−2·091	1·792	3·631*i*	43·72
−10	2	−2·398	1·750	5·857*i*	28·56
	3·2	−2·064	1·792	4·409*i*	23·82
	4	−2·010	1·802	4·033*i*	25·00
	5·33	−1·984	1·807	3·730*i*	28·93
	8	−1·977	1·808	3·508*i*	39·25
0	1	−3·883	1·675	10·579*i*	70·90
	1·33	−3·071	1·706	8·135*i*	45·02
	1·6	−2·694	1·727	6·953*i*	35·22
	2	−2·356	1·756	5·824*i*	27·75
	2·13	−2·279	1·762	5·554*i*	26·28
	2·29	−2·208	1·771	5·292*i*	25·00
	2·67	−2·079	1·787	4·790*i*	23·07
	3·2	−1·977	1·804	4·334*i*	22·18
	4	−1·903	1·817	3·934*i*	22·75
	5·33	−1·858	1·826	3·608*i*	25·78
	8	−1·839	1·832	3·369*i*	34·42
0 (2nd Solutions)	1	−4·602	3·320	11·504*i*	105·00
	1·33	−4·000	3·353	9·362*i*	83·95
	1·6	−3·763	3·370	8·397*i*	78·42
	2	−3·585	3·385	7·543*i*	78·00
	2·67	−3·472	3·396	6·837*i*	85·88
	4	−3·419	3·402	6·316*i*	112·03
	8	−3·405	3·404	6·001*i*	206·28

* Calculated from equations (22).

Each table includes a second series of solutions in which **B** is zero, and these results are plotted for comparative purposes in fig. 6. An indefinite number of such solutions really exists, as in most problems of elastic stability,† but the lowest values of **A** (*i.e.*, of S) predominate in importance. Indeed, from the practical point of view our concern is principally with the minimum value of S for which the frequency of vibration vanishes, because no restriction is imposed upon the wave-length of the displacement in a strip of infinite length.

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* The sentences in square brackets were added March 12, 1924, at the suggestion of a referee, to replace a less simple proof which had been offered by the authors. It will be noticed that the conclusion is unaltered when **C** has a finite value.

† In the same way, an indefinite number of solutions correspond to any finite value of **B**; of these, only those for which **A** has its lowest value have been included in figs. 2 and 3.

17. *Determination of the Normal Modes.*—When a solution of the frequency equations has been obtained in the form of simultaneous values of α, β and γ, it is easy to deduce the corresponding mode—*i.e.*, the nature of the form into which the strip is distorted during the vibration. The tables show that γ is always a pure imaginary quantity, so that, writing

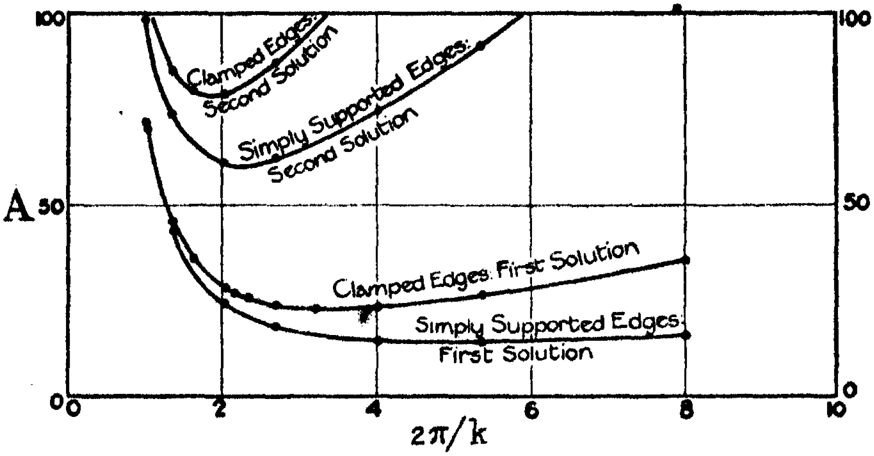

Fig. 6.—First and second solutions for conditions of neutral elastic stability.

$$\gamma = i\delta$$

and substituting from (23) in (18), we have

$$\mathrm{Y} = e^{i\alpha x}(\mathrm{P}e^{i\beta x} + \mathrm{Q}e^{-i\beta x}) + e^{-i\alpha x}(\mathrm{R}e^{-\delta x} + \mathrm{S}e^{\delta x}). \tag{27}$$

Substituting again in (12), we have

$$\mathrm{W} = \sin p\,(t - t_0)\,[e^{i(kx/b + \alpha x)}(\mathrm{P}e^{i\beta x} + \mathrm{Q}e^{-i\beta x}) + e^{i(kx/b - \alpha x)}(\mathrm{R}e^{-\delta x} + \mathrm{S}e^{\delta x})]. \tag{28}$$

Now, if equation (17) is satisfied by values k, λ, it will evidently be satisfied by $-k$, $-\lambda$. Proceeding in exactly the same way as before, we obtain the alternative solution

$$\mathrm{W}' = \sin p\,(t - t_0)\,[e^{-i(kx/b + \alpha x)}(\mathrm{P}e^{-i\beta x} + \mathrm{Q}e^{i\beta x}) + e^{-i(kx/b - \alpha x)}(\mathrm{R}e^{\delta x} + \mathrm{S}e^{-\delta x})], \tag{29}$$

as may be verified by substitution, since the boundary conditions yield the same relations between P, Q, R, S, whether applied to (28) or to (29).

Finally, adding (28) and (29), we obtain a solution of real form, as follows :—

$$\begin{aligned} w &= \mathrm{W} + \mathrm{W}', \\ &= 2\mathrm{P} \sin p\,(t - t_0)\,[\cos\{kx/b + (\alpha + \beta) z\} + \mathrm{K} \cos\{kx/b + (\alpha - \beta) z\} \\ &\qquad + \mathrm{L} \sinh \delta z \sin (kx/b - \alpha z) \\ &\qquad + \mathrm{M} \cosh \delta z \cos (kx/b - \alpha z)], \end{aligned} \tag{30}$$

where K, L and M are constant coefficients, connected with P, Q, R, S by the relations

$$\left.\begin{aligned} \mathrm{PK} &= \mathrm{Q}, \\ \mathrm{PL} &= i\,(\mathrm{S} - \mathrm{R}), \\ \mathrm{PM} &= \mathrm{S} + \mathrm{R}. \end{aligned}\right\} \tag{31}$$

Any arbitrary phase constant can of course be added to x.

The three coefficients K, L, M (which alone are significant, since the absolute magnitude of w is unrestricted) can be determined by means of any three of the four boundary conditions (14) or (15); the remaining condition must then be satisfied, because α, β and γ constitute a solution of the appropriate determinantal equation (19) or (20). When K, L, M are known, we can employ (30) to calculate the form of the displacement.

Calculations have been conducted on these lines to determine, both for simply supported and for clamped edges, the form assumed by the strip when held in a configuration of steady distortion by the smallest shear for which neutral stability can occur. For simply supported edges we have (Table I; **B** = 0)

$$k = \frac{2\pi}{5 \cdot 33}, \quad \alpha = -1 \cdot 445, \quad \beta = 1 \cdot 383, \quad \delta = 2 \cdot 977, \tag{32}$$

and it is found that

$$\mathrm{K} = 0 \cdot 6424, \quad \mathrm{L} = -0 \cdot 0425, \quad \mathrm{M} = 0 \cdot 02129. \tag{33}$$

For clamped edges (Table II; **B** = 0) we have

$$k = \frac{2\pi}{3 \cdot 2}, \quad \alpha = -1 \cdot 977, \quad \beta = 1 \cdot 804, \quad \delta = 4 \cdot 334, \tag{34}$$

and it is found that

$$\mathrm{K} = 0 \cdot 6728, \quad \mathrm{L} = -0 \cdot 0131, \quad \mathrm{M} = -0 \cdot 0008925. \tag{35}$$

The corresponding modes are exhibited in fig. 4, which shows, for the two types of edge constraint, lines of constant displacement under conditions of neutral stability. The numbers attached to the contours are of course merely relative, since, as we have seen, the absolute magnitude of the displacement is indeterminate. The lines of zero displacement divide the strip into compartments wherein the displacement is alternately positive and negative, as indicated by full and dotted contours respectively.

18. *Allowance for Finite Rotatory Inertia.*—The foregoing results for a strip of negligible rotatory inertia (**C** zero) may be employed to obtain corresponding solutions in cases where **C** has a finite value. For it is evident from (24) that any set of values for α, β and γ which constitutes a solution of (25) or (26) for a strip vibrating under conditions defined by the values k, **A** and **B**, with $\mathbf{C} = 0$, will also constitute a solution* for a strip of which the rotatory inertia is finite, if the mode and conditions of vibration are specified by values k', **A**$'$, **B**$'$, **C**$'$ of the quantities defined in (1), where

$$\left.\begin{aligned} 2k'^2 - \mathbf{B}'\mathbf{C}' &= 2k^2, \\ \mathbf{A}'k' &= \mathbf{A}k, \\ k'^4 - \mathbf{B}'(1 + \mathbf{C}'k'^2) &= k^4 - \mathbf{B}. \end{aligned}\right\} \tag{36}$$

Eliminating **B**$'$ from the first and third of these equations, we have

$$\mathbf{B}\mathbf{C}' = (k'^2 - k^2)\{2 + \mathbf{C}'(k'^2 - k^2)\}. \tag{37}$$

Hence, given k', **A**$'$, **C**$'$, we can determine **B**$'$ by trial from figs. 2 or 3. For by the second of (36) we know the value of **A**k, and a line may therefore be drawn on the diagram for which **A**k has this constant value. This line gives one relation between **B** and k, and a second relation between these quantities is afforded by (37); hence **B** and k are determined, and **B**$'$ can be found by substituting for k in the first of (36).

It can also be shown, by eliminating k^2 from the first and third of (36), that

$$\mathbf{B}'\left(1 + \frac{\mathbf{B}'\mathbf{C}'^2}{4}\right) = \mathbf{B}, \tag{38}$$

whence it is clear that the contours in figs. 2 or 3, being lines of constant **B**, will also relate to constant values of **B**$'$ in a strip for which **C**$'$ has a specified value. Thus, knowing **C**$'$, we can relate the quantities **A**$'$ and k' for any required value of **B**$'$, by taking a series of points on the appropriate contour in figs. 2 or 3, and inserting the values of k and **A** so found in the first and second of equations (36). In this way, diagrams similar to figs. 2 and 3 can be constructed for any specified ratio of thickness to breadth of strip; the contours for zero frequency ($\mathbf{B} = 0$) will of course be independent of this ratio.

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[*] It should be noticed that the *mode* of the vibration (*i.e.*, the displacement pattern) will be modified as regards wave-length.

We have seen in §10 that vibrations of complex period cannot occur, whatever be the magnitude of the rotatory inertia. Hence, the quantities $\mathbf{A}'$, $\mathbf{B}'$, $\mathbf{C}'$, k' must necessarily be real, as well as the quantities $\mathbf{A}$, $\mathbf{B}$, k. It follows from the first of the relations (36) that $2k'^2 - \mathbf{B}'\mathbf{C}'$ must be positive, as has been shown already (§14).

19. *Allowance for Uniform Thrust or Tension in Addition to the Shear.*—Similar methods can be employed to obtain, from figs. 2 and 3, solutions applicable to a strip which is subjected to uniform tension or compression (equal in all directions) in addition to the shear considered previously. If the tension acting across the edges of an element of the strip has an intensity $\mathbf{T}$ per unit length of edge, it can be shown that a term $(-\mathbf{T}\nabla_1{}^2 w)$ must be added on the left of equation (4), and it follows that the quantity $(\mathbf{BC} - \mathbf{T}b^2/\mathbf{D})$ must replace the quantity $\mathbf{BC}$ in equations (13), (17) and (24). Hence, as in §18, any set of values for α, β and γ which constitutes a solution of (25) or (26) for a strip vibrating under conditions defined by k, $\mathbf{A}$ and $\mathbf{B}$, with $\mathbf{C} = 0$, will also constitute a solution* for a mode and for conditions of vibration which are defined by k', $\mathbf{A}'$, $\mathbf{B}'$, $\mathbf{C}'$, $\mathbf{T}$, where

$$\left.\begin{aligned} 2k'^2 - \mathbf{B}'\mathbf{C}' + \frac{\mathbf{T}b^2}{\mathbf{D}} &= 2k^2, \\ \mathbf{A}'k' &= \mathbf{A}k, \\ k'^4 - \mathbf{B}'(1 + \mathbf{C}'k'^2) + \frac{\mathbf{T}b^2k'^2}{\mathbf{D}} &= k^4 - \mathbf{B}. \end{aligned}\right\} \tag{39}$$

Thus we may employ the same methods as were used in §18. On the left of (37), $\mathbf{BC}'$ is replaced by $(\mathbf{BC}' - \mathbf{T}b^2/\mathbf{D})$, and for (38) we have

$$\mathbf{B} = \mathbf{B}' + \tfrac{1}{4}\left(\mathbf{B}'\mathbf{C}' - \frac{\mathbf{T}b^2}{\mathbf{D}}\right)^2. \tag{40}$$

The most interesting conditions are those of neutral elastic stability, for which $\mathbf{B}' = 0$. Here we have

$$\mathbf{B} = \tfrac{1}{4}\mathbf{T}^2b^4/\mathbf{D}^2, \tag{41}$$

so that, given $\mathbf{T}$, we can at once determine the contour in figs. 2 or 3 which corresponds to conditions of neutral stability under a tension of this amount. By the first of (39), given k', we can determine the appropriate value of k, and hence, obtaining the value of $\mathbf{A}$ from the diagram, we can calculate $\mathbf{A}'$ from the second of (39). It will be noticed that only positive values of $\mathbf{B}$ are involved, whether $\mathbf{T}$ be positive or negative; the influence of $\mathbf{T}$ upon $\mathbf{A}'$ is exerted mainly through its effect on the ratio k/k'.

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* But *cf.* footnote, §18.

20. *Approximate Solutions by Lord Rayleigh's Method.*—In problems of the kind which is discussed in this paper, much labour can usually be saved, without serious loss of accuracy, by the employment of Lord Rayleigh's method of approximate calculation. The mode of the displacement is assumed, and the frequency is determined from the energy condition

$$\mathrm{V} + \mathrm{T} = \text{const.}, \tag{42}$$

in which V denotes the total increase in potential energy, and T the kinetic energy of the motion, in a vibration of the assumed type. If the appropriate boundary conditions are satisfied,* and if the mode is suitably chosen in other respects, this procedure will result in a close estimate of the gravest frequency natural to the system, and in any event the estimate will be *too high* ; its accuracy may therefore be improved by including one or more arbitrary parameters in the assumed mode, and subsequently adjusting these so as to make the resulting estimate of frequency a minimum.

We have seen in §19 that the effects of uniform tension or compression, acting in addition to the shear, are equivalent to an alteration in the value of the rotatory inertia, and we may therefore confine our attention to the problem treated in §8. The expressions for V and T are :—

$$\mathrm{V} = \tfrac{1}{2}\mathrm{D}\iint\left[(\nabla^2 w)^2 + 2(1-\sigma)\left\{\left(\frac{\partial^2 w}{\partial x\,\partial y}\right)^2 - \frac{\partial^2 w}{\partial x^2}\cdot\frac{\partial^2 w}{\partial y^2}\right\} + \frac{2\mathrm{S}}{\mathrm{D}}\frac{\partial w}{\partial x}\cdot\frac{\partial w}{\partial y}\right]dx\,dy, \tag{43}$$

$$\mathrm{T} = \rho h\iint\left[\left(\frac{\partial w}{\partial t}\right)^2 + \tfrac{1}{3}h^2\left\{\left(\frac{\partial^2 w}{\partial x\,\partial t}\right)^2 + \left(\frac{\partial^2 w}{\partial y\,\partial t}\right)^2\right\}\right]dx\,dy, \tag{44}$$

the integration extending over the whole area of the strip.

It will be noticed that those terms in the integrand of V which involve $(1-\sigma)$ are equivalent to

$$2(1-\sigma)\left\{\frac{\partial}{\partial x}\left(\frac{\partial w}{\partial y}\cdot\frac{\partial^2 w}{\partial x\,\partial y}\right) - \frac{\partial}{\partial y}\left(\frac{\partial^2 w}{\partial x^2}\cdot\frac{\partial w}{\partial y}\right)\right\},$$

and so vanish on integration.

We have to insert in (43) and (44) the simplest expression for w which gives an approximate representation of the normal mode. Fig. 4 suggests the expression

$$w = \mathrm{Y}\sin\left(\frac{kx}{b} + \mathrm{Z}\right)\sin pt, \tag{45}$$

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* *Cf.* footnote, §4.

in which Y and Z are functions of z only (z denoting, as before, the ratio y/b), chosen so as to satisfy the boundary conditions. Any arbitrary phase-constant may of course be added to x or t.

Substituting this expression in (43) and (44), and inserting the results in (42), we obtain an equation which, after introduction of the symbols defined in (1), may be written in the form

$$\mathbf{B}\int_{-1}^{1}[\mathrm{Y}^2+\mathbf{C}\,\{(k^2+\mathrm{Z}'^2)\,\mathrm{Y}^2+\mathrm{Y}'^2\}]\,dz$$

$$=\int_{-1}^{1}[\{\mathrm{Y}''-(k^2+\mathrm{Z}'^2)\,\mathrm{Y}\}^2+(\mathrm{Z}''\mathrm{Y}+2\mathrm{Z}'\mathrm{Y}')^2+2\mathbf{A}k\mathrm{Z}'\mathrm{Y}^2]\,dz. \quad (46)$$

A dash is here used to denote differentiation with respect to z.

We have next to consider the boundary conditions. Substituting from (45) in (5), we see that for simply supported edges (since $\frac{\partial w}{\partial y}$ will *not* vanish at the edges) Y, Y″ and Z′ must vanish when $z=\pm 1$. The conditions for clamped edges will be satisfied if

$$\mathrm{Y}=\mathrm{Y}'=0,\ \text{when}\ z=\pm 1. \qquad (15)\ \textit{bis}$$

For simply supported edges, making the simplest assumptions which will satisfy the foregoing conditions, we write

$$\left.\begin{aligned}\mathrm{Y}&=\cos\tfrac{1}{2}\pi z,\\ \mathrm{Z}&=\lambda\left(z+\frac{1}{\pi}\sin\pi z\right),\end{aligned}\right\} \qquad (47)$$

leaving the constant parameter λ to be determined from the condition for a minimum value of **B**. If $\mathbf{C}=0$ (as was assumed in §16), we have then, from (46),

$$\mathbf{B}=\left(\frac{\pi^2}{4}+k^2\right)^2+5\lambda^2\left(\frac{\pi^2}{4}+k^2\right)+2\pi^2\lambda^2+\frac{63}{8}\lambda^4+3\mathbf{A}k\lambda, \qquad (48)$$

and the condition for a minimum value of **B** is

$$\frac{\partial\mathbf{B}}{\partial\lambda}=10\lambda\left(\frac{\pi^2}{4}+k^2\right)+\frac{63}{2}\lambda^3+4\pi^2\lambda+3\mathbf{A}k=0. \qquad (49)$$

This equation defines **A** in terms of λ, and the corresponding value of **B** is given by

$$\mathbf{B}=\left(\frac{\pi^2}{4}+k^2\right)^2-5\lambda^2\left(\frac{\pi^2}{4}+k^2\right)-2\pi^2\lambda^2-\frac{189}{8}\lambda^4. \qquad (50)$$

The results are exhibited by the dotted contours in fig. 2.[*]

The treatment of clamped edges is a simpler matter, and correspondingly better accuracy can be obtained. Since the boundary conditions (15) impose no restriction upon Z, it is sufficient to write

$$Z = \lambda z, \tag{51}$$

simply, leaving λ to be determined, as before, from the condition for a minimum value of **B**. Equation (46) now assumes the simpler form

$$\mathbf{B}\int_{-1}^{1}[Y^2 + \mathbf{C}\{(k^2+\lambda^2)Y^2 + Y'^2\}]\,dz$$
$$= \int_{-1}^{1}[\{Y'' - (k^2+\lambda^2)Y\}^2 + 4\lambda^2Y'^2 + 2\mathbf{A}k\lambda Y^2]\,dz, \tag{52}$$

and we have

$$\mathbf{B}\{1+\mathbf{C}(k^2+\lambda^2)\} - \{(k^2+\lambda^2)^2 + 2\mathbf{A}k\lambda\}$$
$$= \frac{\int_{-1}^{1}[Y''^2 + \mathrm{L}Y'^2]\,dz}{\int_{-1}^{1}[Y^2 + \mathrm{M}Y'^2]\,dz}, \tag{53}$$

where

$$\mathrm{L} = 2(k^2+3\lambda^2) - \frac{\mathbf{C}\{(k^2+\lambda^2)^2 + 2\mathbf{A}k\lambda\}}{1+\mathbf{C}(k^2+\lambda^2)},$$

$$\mathrm{M} = \frac{\mathbf{C}}{1+\mathbf{C}(k^2+\lambda^2)}.$$

We have now to choose λ and Y so that **B**, as given by (53), has its minimum value; and if we regard λ for the moment as fixed, it follows that we must choose Y so as to make the quantity on the right of (53) a minimum. But this quantity can be shown to represent the frequency of transverse vibration, as calculated by Lord Rayleigh's method from an assumed mode Y, for a rod having unit flexural rigidity and mass per unit length (with rotatory inertia represented by M), and subjected to end tension of amount L. Evidently, then, **B** has its minimum value when Y represents the gravest normal mode in which the rod can vibrate under these conditions: the ends must be taken as clamped, in order that the boundary conditions for Y may be satisfied.

The transverse vibrations of a rod subjected to end tension were treated by exact methods (as a particular case of a more general problem) in a paper cited above.[*] It was found, as was to be expected, that the mode of vibration depended to some extent upon the ratio of the tension to the flexural rigidity; but the results showed the frequency to be given very approximately by Lord Rayleigh's method, if it is assumed that the mode is independent of the end tension, and such that

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[*] *Cf.* §4.

$$\left.\begin{aligned} \int_{-1}^{1} \mathrm{Y}'^2\,dz &= \frac{1\cdot25\pi^2}{4}\int_{-1}^{1} \mathrm{Y}^2\,dz, \\ \int_{-1}^{1} \mathrm{Y}''^2\,dz &= \frac{5\cdot13\pi^4}{16}\int_{-1}^{1} \mathrm{Y}^2\,dz. \end{aligned}\right\} \tag{54}$$

We may conclude that this assumption will give equally good approximation when applied to (52). When **C** = 0 (as was assumed in §16), the resulting formula is

$$\mathbf{B} = (k^2 + \lambda^2)^2 + 2\mathbf{A}k\lambda + 31\cdot2 + 6\cdot168\,(k^2 + 3\lambda^2), \tag{55}$$

and the condition for a minimum value of **B** is

$$\frac{\partial \mathbf{B}}{\partial \lambda} = 4\lambda\,(k^2 + \lambda^2) + 2\mathbf{A}k + 37\cdot008\,\lambda = 0. \tag{56}$$

This equation defines **A** in terms of λ, and the corresponding value of **B** is given by

$$\mathbf{B} = 31\cdot2 + (k^2 - 3\lambda^2)\,(k^2 + \lambda^2 + 6\cdot168). \tag{57}$$

The results are exhibited by the dotted contours in fig. 3.[†]

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[*] See footnote, §13; the periods of transverse vibration and of "whirling" are in this case identical. Rotatory inertia was neglected in the investigation cited; but since it is equivalent in its effects to an alteration in the end tension, the conclusion drawn above is not invalidated.

[†] *Cf.* §4.

Researches on the Chemistry of Coal.—Part III. The Extraction of Coals by Benzene under Pressure.

By William A. Bone, D.Sc., Ph.D., F.R.S., A. R. Pearson, M.Sc., LL.B., and R. Quarendon, B.Sc., A.R.C.S.

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Introduction.

In the last paper of this series* a new method was described, consisting essentially of a pyridine-amyl alcohol treatment, for extracting and isolating the "resins" present in bituminous coals. It was also shown that they do not usually much exceed 1 per cent. of the coal substance, and that, although doubtless a contributing factor, they are not the chief cause of the coking propensities of such coals. On the contrary, the principal binding power was found to reside in a certain group (provisionally termed "humic" substances) of non-resinous bodies, probably of cellulosic type and origin, whose fusion temperatures are below those at which they undergo rapid decomposition. They may amount to as much as 4 per cent. (or even more) of the coal substance in the case of strongly coking coals. Further, it was suggested that, although perhaps not necessarily existing in the free state in the original coal, possibly they may be present in a state of loose combination therein, from which they can be liberated by a moderate degree of heat.

The use of pyridine, even when largely diluted with some other solvent, for extracting the coal substance, is admittedly open to criticism on the ground of its possible chemical action; and whilst we have always felt that its replacement by a more neutral solvent would be advantageous in many ways, the difficulty has been to find one which will extract the coal to a sufficient degree of completion in a reasonable time. By employing benzene under pressure this difficulty has now been overcome, and the present paper contains an account of our recent experiments in this direction.

Benzene was selected as a neutral solvent which is reasonably stable, at least up to its critical temperature (288° C.); and although its action is very slow when employed at its boiling point under atmospheric pressure in a Soxhlet apparatus, it may be quickened by using higher pressures and temperatures.

Some years ago Fischer and Gluud performed experiments in which coals were extracted by heating them with benzene in a steel bomb at 275° C. under 55 atms. pressure*; but from our recent experiments it seems probable that their extracts underwent some degree of thermal decomposition through being deposited from the saturated solution in contact with the hot walls of the bomb. Indeed, Fischer and Gluud themselves considered that a more satisfactory operation might have resulted had their apparatus enabled them to conduct it on the Soxhlet principle; and they remarked upon the difficulty of constructing an apparatus to work on such principle at high pressures. We have succeeded in overcoming this difficulty by constructing an apparatus which operates on the automatic Soxhlet principle under pressures up to 700 lbs. per square inch.

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* 'Proc. Roy. Soc.,' A, vol. 100, p. 582 (1922).

Fischer and Gluud's extractions were carried out in a steel bomb (162 cm. long and 12 cm. internal diameter with walls 2 cm. thick) capable of withstanding a pressure of 200 atmospheres. Each charge of coal (1 to 2 kilograms broken to the size of hazel nuts) was extracted with from 3 to 3½ litres of benzene, heat being applied to the bomb externally by means of a powerful triple burner surrounded by a sheet-iron cylinder to concentrate the heat as far as possible. The temperature was gradually raised to 275° C. (corresponding with a pressure of about 55 atmospheres), and maintained at such degree for an hour, after which the heat was cut off and the bomb allowed to cool slowly. Each sample of coal was repeatedly extracted in this manner. Finally, the resulting benzene solution, which had a strong green fluorescence in reflected light, and a dark port-wine colour when viewed in thin layers by transmitted light, was distilled on the water-bath (under a pressure of 200 mm. at the finish) and the residual extract weighed.

As a typical example of their results, it may be stated that an Osterfeld bituminous coal ("Steinkohle"), which on repeated extraction with boiling benzene at atmospheric pressure in a reflux apparatus had yielded only 0·1 per cent. of extract, yielded as much as 6·5 per cent. under the foregoing treatment. Rather more than half of it consisted of a brown powder, insoluble in light petroleum, which softened at 140° and melted at 150° C.; the remainder, which was soluble in light petroleum, consisted of a viscous reddish yellow fatty oil. The residual extracted coal had not materially altered in appearance, although it had lost some of its lustre and internal cohesion.

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* 'Ber. Deut. Chem. Ges.,' vol. 49, pp. 1460–1468 (1916).

A.—*The Apparatus and Method of Extraction.*

Our apparatus (fig. 1) consists of a cylindrical steel container A, 27½ ins. inside depth and 4½ ins. diameter, of about 7 litres capacity, the lower half

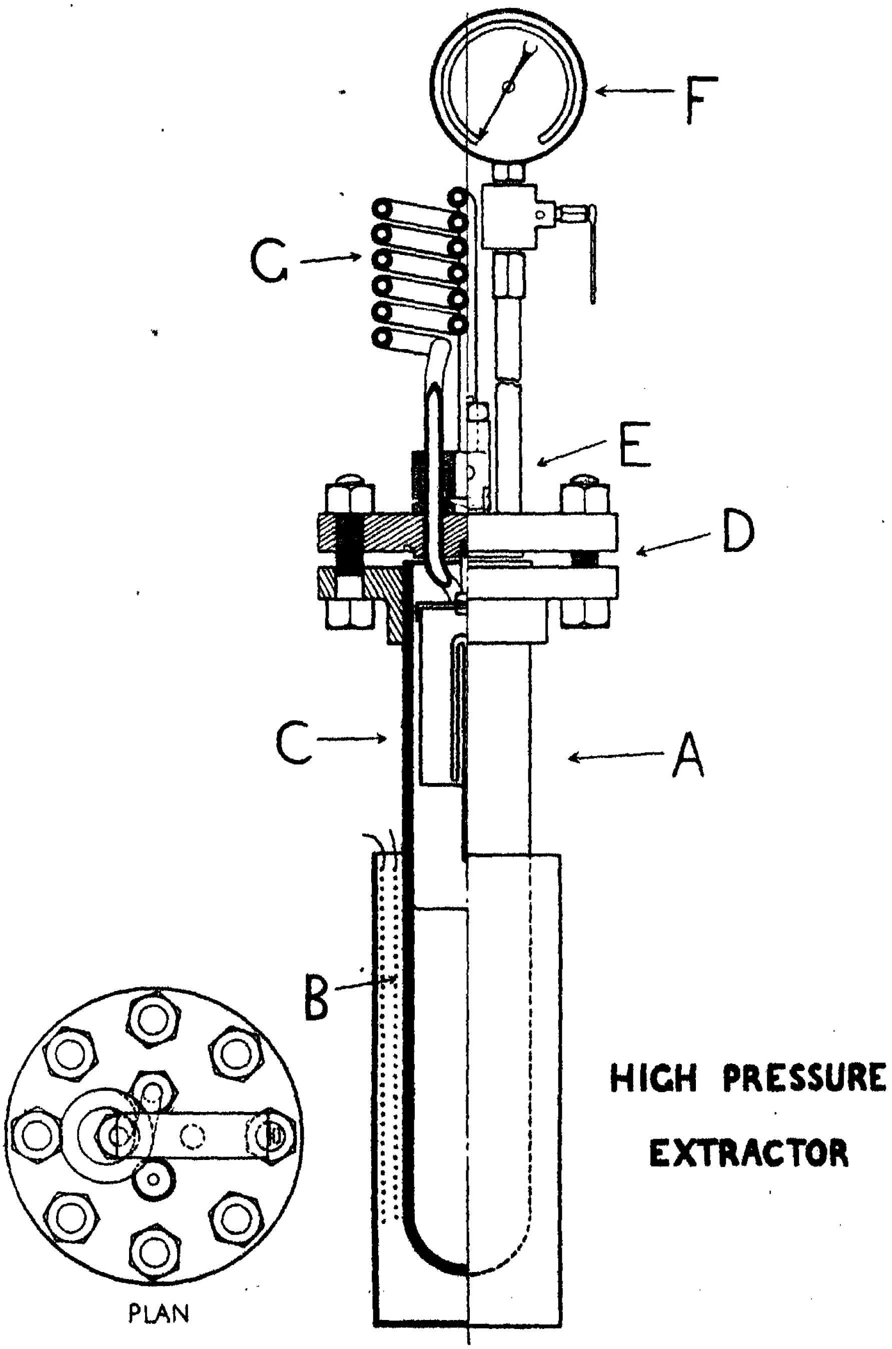

Fig. 1.

of which contains the solvent, and is heated electrically by external coils, B, of nichrome wire. About 500 grams of the coal under treatment are placed above the solvent in a cylindrical cup, C, which is provided with a Soxhlet siphon tube. The container is closed by a flat steel cover, D, bolted to a flange round the top of the cylinder, the joint being made tight by means of a lead ring. This cover carries (*a*) a safety valve, E; (*b*) pressure gauge, F; and (*c*) the two ends of a closed steel condenser coil, G. The vapour from the hot solvent ascends the shorter limb of this condenser, and in passing downwards through the spiral part is condensed, the resultant liquid falling into the siphoning cup C. The dimensions of the apparatus are calculated to give four or five siphonings per hour when 500 grams of coal are being extracted at pressures of from 250 lbs. to about 700 lbs. per square inch, which are the limits of the practical working range of the apparatus.

In carrying out the extraction of a coal, a representative sample of it was first of all ground until it would pass through a sieve of 20 meshes, but not one of 40 meshes, to the linear inch. After being thoroughly dried in a vacuum steam oven at 80° to 100° C., about 500 grams of it were placed in a receptacle made of iron-wire gauze of 100 meshes to the linear inch, which just fitted into the siphoning cup C of the extraction apparatus. About 3½ litres of pure, dry benzene were employed as the solvent. The extraction apparatus when so charged was evacuated by a Fleuss pump, and its benzene container was then gradually heated electrically up to the desired temperature.

The extraction was then allowed to proceed in successive stages, each of which usually extended continuously over a period of from five to six days. During the first of these stages the apparatus was run at a pressure of 250 lbs. per square inch (corresponding with a temperature of 240° C.). The second stage was usually run at a pressure of 500 lbs. per square inch (temperature 260° C.), whilst the third was run at a pressure of 700 lbs. per square inch (temperature 285° C.).* Between each stage the container was opened and the solution therein removed and replaced by fresh solvent.

By such procedure the coal was fractionally extracted by the solvent at each of three definite pressures (and consequently temperatures), and the portion extracted during each stage retained for subsequent examination. Generally speaking, the greater part of the extract was obtained during the first stage; another considerable proportion was obtained during the second stage, but comparatively little resulted from the third stage. In the end the extraction was complete at the pressure indicated.

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* These pressures were approximate only, being sometimes varied within 50 lbs. per square inch on either side, according to the coal employed or other circumstances.

It may be observed that, in regard to the various bituminous and semi-bituminous coals examined, in no case was any sign of gas-evolution observed, although a small quantity (probably not exceeding 1 c.c.) of water was eliminated from the coal substance during the long extraction process. It is therefore clear that in such cases no material decomposition of the coal substance occurred. Moreover, our experiments have satisfied us that such a "Soxhlet extraction" is much superior to the method described by Fischer and Gluud, where the liquid was continuously in contact with the coal substance; because we have found that the complex substances extracted by benzene under such conditions, if left in contact with the residual mass, are liable to undergo chemical changes (polymerisation and condensation), whereby they become insoluble. Obviously also, the apparatus in question might be used in similar fashion for extraction with solvents other than benzene.

As might be expected, a much larger proportion of the coal substance is extractable by benzene at the higher pressures employed by us than with the same solvent at atmospheric pressure. Thus, in the case of the bituminous caking coals examined, the portion of the coal substance extracted at high pressures amounted to between 7 and 11 per cent., according to the coal, as compared with from 1·2 to 3·3 per cent. at ordinary pressure. Moreover, whereas after the latter process the coking propensities remained practically unimpaired, after the former they had almost entirely disappeared. It is thus evident that the constituents of the coal which confer coking properties upon it are extractable by benzene under the conditions employed by us. Hence the method described herein is one which allows of the removal of the "coking constituents" of coal without employing a medium like pyridine, which undoubtedly has a considerable depolymerising action upon the coal substance in addition to its ordinary solvent action.

B.—*Treatment of the Crude Extract from Bituminous Caking Coals.*

The four bituminous caking coals examined in this connection were selected from among those previously employed for the work described in Parts I and II hereof, and were as follows:—

A. The Durham hard-coking coal.

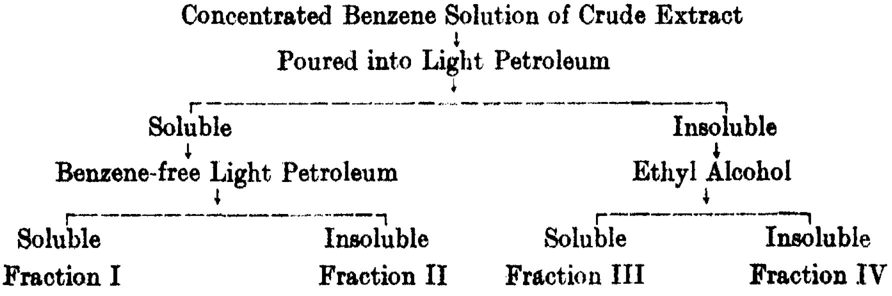
B. The Barnsley steam coal, yielding a moderately hard coke, from Brodsworth colliery.

C. One of the two Spanish coking coals from adjacent seams (called Nos. IV and V respectively), of carboniferous age, near the towns of Ponferrada and Villablino in the province of Leon (North Spain).

F. The South Wales hard-coking coal.

Full details as to the ultimate compositions of these coals are shown in Table I hereof.

The benzene solutions yielded by the foregoing coals were deep red-brown in colour, with a marked greenish fluorescence. They were first of all concentrated by distillation until incipient separation of the dissolved extract was noticed. The residual hot liquid was thereupon poured into about five times its volume of light petroleum (b.p. 40° to 60° C.) which had the effect of retaining in solution certain wax-like constituents of the crude extract, and of precipitating the remainder of it. The soluble part was again separated into two portions according as it was soluble or not in benzene-free light petroleum. The insoluble part was subsequently extracted in a Soxhlet apparatus with alcohol which removed resinous bodies. The scheme of fractionisation is diagrammatically shown below.



By such procedure the crude extract from each coal was resolved into four fractions as follows :—

(I) A yellow-brown non-nitrogenous portion soluble in light petroleum.

(II) A nitrogenous red-brown solid, of low softening point, soluble in a mixture of 4 parts light petroleum and 1 part benzene.

(III) A non-nitrogenous resinous portion.

(IV) A group of nitrogenous bodies of "humic" type.

These will now be described in greater detail; the quantitative results of the benzene extraction, as well as the ultimate compositions of the various fractions obtained are shown in Table I. It should be particularly noted that they were all easily soluble in chloroform, a circumstance which differentiates

Table I.

Coal.	A (Durham).				B (Barnsley).				C (Spanish).				F (Welsh).			
	Dry.		Dry, Ashless.		Dry.		Dry, Ashless.		Dry.		Dry, Ashless.		Dry.		Dry, Ashless.	
Ultimate Analyses of Coals C	82·73		85·07		82·33		84·68		78·30		86·28		82·58		85·90	
H	4·76		4·90		4·99		5·13		4·30		4·74		4·56		4·74	
N	1·09		1·12		1·50		1·54		1·40		1·54		0·94		0·98	
S	1·28		1·32		0·70		0·72		0·75		0·83		0·47		0·49	
O	(diff.) 7·38		7·59		7·72		7·93		6·00		6·61		7·59		7·89	
Ash	2·76		—		2·76		—		9·25		—		3·86		—	
	100·00		100·00		100·00		100·00		100·00		100·00		100·00		100·00	
Volatiles evolved at 900°C. (per cent.)	26·3		27·0		32·2		33·1		19·6		21·7		21·7		22·6	
Character of Coke.	Dense and very hard.				Hard.				Dense and very hard.				Hard and very dense.			
Yield of Extracts (p. cent.)*	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV
	1·9	1·7	0·8	7·0	2·2	0·6	0·4	5·1	3·9	0·2	0·7	4·6	1·3	1·1	0·3	5·1
Yield of Total Extract (p. cent.)*	11·4				8·3				9·4				7·8			
Ultimate Analyses of Extracts C	87·94	82·84	84·39	87·52	88·72	81·34	83·75	86·68	87·93	Not analysed	86·58	88·49	89·66	87·77	83·68	88·32
H	8·89	6·33	6·77	5·63	8·96	6·87	7·00	5·67	9·22		7·79	5·88	8·06	6·27	6·55	5·40
N	—	0·36	—	1·22	—	0·96	—	1·51	—		1·70	1·20	—	0·70	—	1·12
S	—	1·90	—	0·43	—	0·59	—	2·66	—		0·33	0·94	—	1·10	—	0·14
O	3·17 (diff.)	8·57	8·84	5·20	2·32	10·24	9·25	3·48	2·85		3·60	3·49	2·28	4·16	9·77	5·02
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00		100·00	100·00	100·00	100·00	100·00	100·00

* Calculated on dry, ashless coal substance.

them from the pyridine extracts obtained from such coals which are always only partly soluble in chloroform.

Fraction I was in all cases composed of soft non-nitrogenous wax- or vaseline-like substances closely resembling those similarly obtained from the crude pyridine amyl-alcohol extract during the course of our previous work (*q.v.* p. 592). The amounts obtained varied between 1·3 per cent. of the whole coal substance in the case of the Welsh coal F, to as much as 3·9 per cent. in the case of the Spanish coal C; the other two coals each yielded about 2 per cent. They were all quite free from nitrogen and sulphur. Their ultimate compositions, which were all nearly the same, closely approximated to that of a hydrocarbon, as follows:—

C = 87·9 to 89·7; H = 8·1 to 9·2; O (by diff.) = 2·3 to 3·2 per cent.

Perhaps the most important feature of their properties is that, so far as could be judged from the testing method outlined in our previous paper (*loc. cit.*, p. 595), they had *per se* no influence whatever upon the coking propensities of the coals.

Fraction II was in all cases a reddish-brown solid of low softening point (about 25° C.), which like Fraction I was apparently without any influence upon the coking propensities of the coal. The amounts obtained were always less, and sometimes considerably less, than those of Fraction I, varying between 0·2 per cent. of the whole coal substance in the case of the Spanish coal C and about 1·7 per cent. in the case of the Durham coal A. In no case was this fraction free from either nitrogen or sulphur, and the ultimate compositions (Table I) showed much greater variations than was the case with Fraction I.

Fraction III was in all cases composed of reddish-brown brittle resinous substances, substantially free from nitrogen and sulphur, with softening-point about 60° C., resembling the resinous part of the pyridine amyl-alcohol extract described in our previous paper (*q.v.*, p. 595). The amounts obtained varied from about 0·3 per cent. of the coal substance in the case of the Welsh coal F up to 0·8 per cent. in the case of the Durham coal A. The ultimate compositions (except in the case of that from the Spanish coal C which was obviously contaminated with nitrogenous bodies) varied between the following limits:—

C = 83·7 to 84·4; H = 6·6 to 7·0; O = 8·8 to 10·1 per cent.,

which are very near to the composition of the pure resin obtained from the same coals, referred to in the previous paper of the series, namely:

C = 82·15; H = 7·11; O = 10·74.

Also, like it, these substances all had a marked binding power upon dry pulverised coke when tested by the method described on p. 595 of the previous paper (*q.v.*), and must therefore be considered as being a contributory factor to (though not the chief cause of) the coking propensities of the coals. It may here be remarked that in the previous paper (p. 597) it was concluded that the resins present in such strong coking coals as A and B, "probably do not normally much exceed 1 per cent. of the coal substance"; but in the light of our present results, this would seem to be rather an over-estimate. We would now consider it probably more correct to say that they are normally present in amounts not exceeding 1 per cent.

Fraction IV always consisted of amorphous cinnamon-brown powders containing between 1·12 and 1·50 per cent. of nitrogen as well as from 0·4 to 0·9 per cent. of sulphur. They formed colloidal solutions with benzene, as distinguished from the true solutions similarly formed by the bodies comprising the two fractions I and III; and indeed they could be separated from the said other two fractions by dialysing their benzene solutions through a collodion membrane. Their softening points, which varied between 185 and 230° C., were also much higher than those of any of the other three fractions; and their ultimate compositions all fell within the following narrow limits :—

$$\mathrm{C} = 86{\cdot}68 \text{ to } 88{\cdot}50,\ \mathrm{H} = 5{\cdot}40 \text{ to } 5{\cdot}88,\ \mathrm{N} = 1{\cdot}12 \text{ to } 1{\cdot}50,\ \mathrm{S} = 0{\cdot}4 \text{ to } 0{\cdot}9,$$
$$\text{and O (by diff.)} = 3{\cdot}15 \text{ to } 4{\cdot}88 \text{ per cent.}$$

The considerable amounts of nitrogen invariably present in these substances, as well as their properties generally, indicate that they have no relation to coal-resins, but rather that they are of a "humic" type, possibly derived from an amalgamation of proteid and cellulosic transformation products. Be that as it may, they certainly had a very strong binding power upon the coal when tested by our method. The amounts of them obtained from the three coals B, C and F were nearly the same, namely, between 4·6 and 5·1 per cent. of the coal substance; but in the case of the Durham coking coal A it was as much as 7·0 per cent. Indeed, according to our experience up to the present, the relative agglutinative powers of a series of bituminous coals run nearly parallel to their yields of this fraction. And, therefore, our previous conclusion that such bodies must be considered as the chief cause of the coking propensities of bituminous coals has thus been confirmed.

The *residues* from our benzene extractions were almost, though not quite, devoid of coking properties; they still retained a certain tendency to sinter, but showed no sign whatever of intumescing on being carbonised at 900° C. Also, their cohesive powers at ordinary temperatures were much inferior to those of the respective coals from which they had been derived. From this it may be concluded that, although the coke-producing constituents of a coal are non-extractable by benzene at its boiling point under atmospheric pressure, they are practically all removable by it under the conditions employed by us. It should also be stated that on mixing these residues intimately with the Fraction IV (*i.e.*, the main "coking constituents") in the proper proportions corresponding with the original coals, nothing like the strongly coking propensities of the latter were reproduced; neither did the resulting mixtures visibly intumesce on being carbonised. It would thus seem as though some factor other than the mere intimate association of the chief coking constituents with the residues is required to develop fully the coking propensities of the coals; but this is a matter requiring further investigation.

C.—*The Extraction of Semi-bituminous Coals.*

During the course of our investigation the two typical non-coking semi-bituminous coals—the Spanish coal E (volatiles = 17·9 per cent.) and the South Wales coal G (volatiles = 10·2 per cent.)—described in the previous paper of this series, were extracted in our apparatus, without, however, any very material result. Thus the Spanish coal E yielded no more than 0·48 per cent. of total extract after 24 days' treatment with benzene (namely, 14 days at 300 lbs. per square inch *plus* 10 days at 500 lbs. per square inch), whilst the South Wales coal G similarly gave only 1·25 per cent. It would, therefore, seem that the non-coking characters of such semi-bituminous coals may be ascribed to their comparatively small contents of constituents extractable by benzene at such pressures.

In this connection it may be recalled that the non-coking semi-bituminous Spanish coal E (volatiles = 17·9 per cent.) which contained only 0·48 per cent. of extractable constituents, came from a seam (0·5 metre thick) only a few metres away from another parallel seam (2 metres thick) of a good bituminous coking coal D (volatiles = 22·7 per cent.) yielding about 8 per cent. of total extract, five-eighths of which comprised the "coking constituents." Also, the known occurrence of porphyritic rock in the roof of the seam E, and its non-occurrence above the neighbouring seam D, strongly indicate that the semi-bituminous and non-coking character of the former has been the result of some igneous intrusion subsequent to the formation of the seam. And our experiments would lead us to conclude that the chief effect of such igneous intrusion upon the original coal (which presumably was bituminous, like all the other seams in its neighbourhood) had been to expel from it the greater part of these benzene-extractable constituents, thus transforming it into a semi-bituminous non-coking type of coal. Indeed, the occurrence of such a non-coking "semi-bituminous" coal under a roof of porphyritic rock, in parallel between two closely adjacent seams, both of hard coking coals without any such porphyritic covering, taken in conjunction with our observations regarding their strikingly different behaviours when extracted with benzene in our apparatus, seems to us to be a convincing piece of evidence as to the actual conversion of a bituminous into a semi-bituminous coal as the result of such igneous intrusion.

D.—*Extraction of Sub-bituminous Coals.*

We next investigated two interesting coals of the sub-bituminous genus, one of them (K) of Nigerian origin with feebly caking properties, and the other (L) from Kaitangata, New Zealand, which was quite devoid of them. Both were well-matured fuels of lignitic type, the New Zealand coal having a black, lustrous and vitreous appearance, with a distinctly laminated structure and, in places, conchoidal fracture. The ultimate compositions of the respective dry-ashless coal substances were as follows:—

	K.	L.
	Per cent.	Per cent.
Carbon	78·77	71·70
Hydrogen	5·55	5·60
Nitrogen	1·63	1·20
Sulphur	1·50	0·30
Oxygen (by diff.)	12·55	21·20
Per cent. volatiles yielded at 900° C.	45·0	45·4

The benzene extraction was carried out, in the case of the Nigerian coal, for 15 days altogether, in three stages, namely, at 250, 400 and 500 lbs. per square inch pressure respectively; but in the case of the New Zealand coal, for 20 days in three stages, namely, at 280, 400 and 600 lbs. per square inch respectively. It is to be noted that although in the long run the New Zealand coal yielded a larger amount of extract (7·8 per cent.) than did the Nigerian coal (5·0 per cent.), practically none of it was obtained during the first of the three extraction stages; on the other hand, the Nigerian coal yielded a considerable portion of the total extract in the first stage.

On fractionating the crude extracts in the manner described on pp. 613–615 hereof, they were respectively resolved into the following portions:—

	K.	L.
	Per cent. on dry ashless Coal-Substances.	
Fraction I (wax-like)	1·8	2·9
Fraction II	0·3	1·7
Fraction III (resinous)	0·8	2·4
Fraction IV (Humic)	2·1	1·2
Totals	5·0	8·2

In outward appearance and general physical behaviour all these fractions closely resembled the corresponding ones obtained from the four bituminous coals described in section B hereof; also the "resinous" and "humic" fractions III and IV had much the same binding powers upon dry pulverised coke as the bituminous coal fractions III and IV, when tested by our method. The following results of chemical analyses showed that whilst their ultimate compositions (see below) generally resembled those of the corresponding bituminous coal fractions, all of them contained proportionately less carbon but more oxygen and hydrogen than the latter; and this more particularly applied to fractions III and IV. The "resinous" fractions III were readily soluble in a cold dilute solution of potassium hydroxide and fractions I slightly so; but the other two fractions were not acted upon by the alkali.

	Fraction I.		*Fraction II.*		*Fraction III.*		*Fraction IV.*	
	K.	L.	K.	L.	K.	L.	K.	L.
Carbon	85·30	83·30	82·65	78·80	77·15	76·25	82·45	79·90
Hydrogen	10·10	10·80	9·75	11·75	7·30	7·20	7·00	7·70
Nitrogen	Nil	Nil	Not determined	0·30	Nil	Nil	1·30	0·80
Sulphur	Nil	0·35	—	0·65	Nil	Nil	Nil	4·05
Oxygen (diff.)	4·60	5·55	—	8·50	15·55	16·55	9·25	7·55
	100·00	100·00	—	100·00	100·00	100·00	100·00	100·00

It should be observed that these two coals both contained much smaller total amounts of the two binding-constitutentes III and IV than any of the four caking bituminous coals investigated; and doubtless it is to this circumstance that their comparatively non-coking characters are to be ascribed. Singularly enough, although the New Zealand coal L contained much more of the "resinous" fraction III than any other of the coals examined, it was quite devoid of coking propensities.

In neither case had the residues remaining after the benzene extraction any coking propensities; but on intimately mixing them with about 5 per cent. of the "coking constituents" (Fraction IV) from the bituminous coking coals investigated, and subsequently carbonising the mixtures, weak cokes were obtained in each case. This circumstance again indicates that the full development of the coking propensities of a coal depends on the co-operation of some factor other than the mere intimate association of its chief coking constituents with its benzene-extracted residue.

E.—*Extraction of Morwell Brown Coal.*

So far we have considered only such coal types as, chemically speaking, may be regarded as matured; and the differences between them are due rather to differences between the relative contents of the corresponding fractions (and especially II and IV) of the benzene extracts described herein, than to any marked dissimilarities between those fractions.

We now propose to deal with the behaviour of an immature brown coal when extracted with benzene under the conditions we have employed. For this part of our investigation we selected the well-known tertiary Morwell Brown Coal, from the Gippsland region of the State of Victoria in Australia.

Morwell lies in or near the Latrobe Valley, about 90 miles from Melbourne, where extensive faulting seems to have taken place towards the end of the Miocene period, producing the enormous depression in which large accumulations of vegetable débris were subsequently deposited during Pliocene times, whence originated the brown coals of that region. It has been estimated that within an area of 50 square miles in the Latrobe Valley, and within 1,000 feet of the surface, there are 31,144 million tons of the coal; and a bore-hole put down by the Victorian Government near Morwell, disclosed within 1,019 feet of the surface no fewer than seven beds of brown coal, of a total thickness of 781 feet. The uppermost bed, which is at present being utilised for the great electric power scheme which the Victorian State Electricity Commissioners are now developing, consists of a matrix of earthy-brown coal, with sporadic inclusions of lignite. Under the microscope the matrix itself appears to consist of pollen grains, spore cases, and remains of cutinised leaf tissue without any actual woody-fibre. In the raw state the coal contains rather more than 50 per cent. of water, and a small amount of mineral matter. The dry "ashless" coal substance contains:—

$C = 65 \cdot 10$, $H = 5 \cdot 00$, N and $S = 0 \cdot 45$, and $O = 29 \cdot 45$ per cent.;

and, on being carbonised at 900° C., it yields 57·6 per cent. of volatiles. In view of its typical character as an immature earthy brown coal and of its economic importance to Australia, its further scientific investigation is of considerable interest.

It had already been proved by one of us* that at temperatures beginning as low as 130° C., but principally between 250° and 375° C., the cellulosic or humic constituents of the dry coal undergo an internal condensation characterised by the simultaneous elimination of steam and carbon dioxide, without any appearance whatever of oils or more than a quite negligible amount of gaseous hydrocarbons or hydrogen. We were, therefore, not surprised to find that, on extracting the dry coal with benzene for a period of 3 to 10 days continuously, at pressures up to 600–700 lbs. per square inch (corresponding to temperatures of 250° to 280° C.), some water together with a gas containing about 86·2 per cent. of carbon dioxide and 8·5 per cent. of carbon monoxide, was always found in the apparatus at the end of the experiment. Such internal "condensation" of cellulosic aggregates presumably would not involve any real breakdown of their molecular constitution.

In each of our experiments, about 300 grms. of coal, previously completely dried in a vacuum-steam oven and ground to pass through a sieve of 20, but not through one of 40 meshes to the linear inch, were extracted in the apparatus with 3½ litres of benzene for a period of 10–12 days continuously. The extracted matter usually amounted to about 15 per cent. of the weight of the "dry-ashless" coal substance taken; the residue was almost entirely soluble in an aqueous solution of potassium hydroxide, from which solution it could be recovered on acidification as a dark brown flocculent precipitate.

F.—*Treatment of the Benzene Extracts.*

The benzene solutions, which were reddish-brown in colour, with a strong greenish fluorescence, were handled in a quite different way from those obtained in corresponding experiments with the bituminous coals, because of the markedly different character of the extract contained therein, which was found to be resolvable into acidic, saponifiable, and neutral portions, in the following manner:—

The resulting benzene solution, having been concentrated to about one-third of its original bulk by distillation, was agitated in the cold with a 5 per cent. aqueous solution of potassium hydroxide, and then left some days in contact with it. This procedure caused an immediate precipitation of flocculent matter, and ultimately there separated out a brown turbid aqueous layer, which darkened somewhat in colour with time, and contained acidic matter in suspension as well as in solution. The benzene solution, which was quite free from suspended matter, having been drawn off from the said aqueous layer, was next boiled in a reflux apparatus for about six hours with one-tenth its volume of a normal alcoholic potash solution in order to hydrolyse any esters present. Water was then added to the cooled liquid until a separation into two layers resulted. The turbid aqueous-alcoholic layer having been removed, the treatment of the remaining benzene solution with alcoholic potash was repeated, when the action of the alkali appeared to be complete.

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* 'Proc. Roy. Soc.,' A, vol. 99, pp. 236 to 252 (1921).

(*a*) *The Non-acidic and Unsaponifiable Resene-like Portion.*—The benzene solution, having been thoroughly washed with water, was next dried, and the solvent distilled off. After cooling, the residue set to a deep red solid, which analysis showed to have the following percentage composition :—

$$C = 83 \cdot 85, \quad H = 10 \cdot 40, \quad N = \text{trace}, \quad S = \text{nil}, \quad O = 5 \cdot 75.$$

In order to ensure that all hydrolysable matter had been eliminated from it, it was redissolved in dry benzene, and the solution boiled for 6 hours in a reflux apparatus with an alcoholic solution of sodium ethoxide. On thoroughly washing the resultant liquid mixture with water, a very small quantity of reddish matter was removed from it; but eventually the greater part of the material was recovered unchanged from the benzene solution as a deep red brittle mass of resinous appearance, which subsequent analysis showed to be now quite free from either nitrogen and sulphur, and to have the following ultimate composition :—

$$C = 84 \cdot 85, \quad H = 10 \cdot 40, \quad O \text{ (by diff.)} = 4 \cdot 75 \text{ per cent.}$$

The amount of this unsaponifiable fraction so obtained, which seemed to be a resene-like substance, and which had only a slight binding power, was equal to between 5 and 6 per cent. of the dry ashless coal substance originally taken.

(*b*) *Resin-Ester Portion.*—The aqueous alcoholic washings obtained as the result of the before-mentioned sodium ethoxide treatment yielded after acidification a small quantity of a light brown material amounting in all to about 0·65 per cent. of the original coal substance; it seemed to be resinous, and presumably had existed in the coal as a resin-ester. It had the following ultimate composition :—

$$C = 76 \cdot 25, \quad H = 8 \cdot 75, \quad O \text{ (by diff.)} = 15 \cdot 00 \text{ per cent.}$$

(*c*) *Aliphatic or Alicyclic Acid and Ester Portion.*—The alkaline liquids resulting from the foregoing aqueous and alcoholic-potash treatments were mixed together and distilled until most of the alcohol had been got rid of. The residual liquid was then acidified with aqueous hydrochloric acid, and heated, when a flocculent precipitate appeared, which melted before the liquid had reached its boiling point, and after cooling remained on the surface as a dark brown brittle cake with conchoidal fracture. After being dried *in vacuo* its composition was :—

$$C = 78 \cdot 00,\ H = 7 \cdot 00,\ N = 0 \cdot 25,\ S = \text{nil},\ O = (\text{by diff.}),\ 14 \cdot 75 \text{ per cent.};$$

and the quantity recovered amounted to about 8 per cent. of the original coal substance. The material which on subsequent investigation seemed to be a mixture of complex wax-like acids, was readily soluble in benzene, chloroform, ethyl alcohol (95 per cent.) or ether. Its alkaline solutions frothed readily like soap solutions. On being heated it melted and intumesced, giving off steam and heavy vapours having a fatty (as distinct from an aromatic) odour; and on being heated with soda-lime under reduced pressure up to 380° C. it yielded about one-fifth of its weight of a yellow wax of a buttery consistency, whose ultimate composition ($C = 86 \cdot 45$, $H = 12 \cdot 40$, $O = 1 \cdot 15$ per cent.) was nearly that of a hydrocarbon. These observations, which need to be extended before any final conclusion can be drawn, seem to indicate that the acidic substances mainly comprised in this fraction of the benzene extract had an aliphatic or alicyclic structure, and had comprised both free acids and their esters.

It should also be mentioned that, when carbonised in admixture with nine times their weight of coke dust, these substances exhibited considerable binding powers, the resulting coke having a crushing strength of 120 to 140 lbs. per square inch when tested by the method described in the previous paper of this series (p. 595, *q.v.*). This circumstance is the more remarkable because the original dry brown coal from which they were derived exhibited no vestige whatever of coking propensities.

(*d*) *Polyhydroxy-phenols.*—On saturating with bromine the aqueous liquor remaining after the acidic substances described under (*c*) had been removed, minute oily particles separated, which after a while coalesced into a crystalline precipitate composed of fine yellow needles. The total yield of them was very small, however, amounting to no more than 0·2 per cent. of the original dry coal substance. On further investigation they proved to consist partly of *tribrom-pyrogallol* $C_6Br_3(OH)_3$ and partly of a *tribrom-methyl di-hydroxy-benzene* $C_6Br_3(OH)_2CH_3$. It is thus evident that the acidic part of our benzene extract contained small quantities of pyrogallol and methyl-dihydroxy-benzene which possibly are to be regarded as products of some incipient thermal decomposition which occurred during the long benzene extraction process.

We had thus succeeded in resolving the original benzene extract (amounting to about 15 per cent. of the original coal substance) into four distinct fractions :—

	Per Cent. on original Coal Substance.
(*a*) Unsaponifiable resene-like portion	5 to 6
(*b*) Resin esters	0·7
(*c*) Aliphatic or alicyclic acids and esters	8 to 9
(*d*) Polyhydroxy-phenols	Almost negligible.

The complete elucidation of the precise characters and constitutions of the very interesting substances comprised under (*a*) and (*c*), which together formed by far the greater part of the whole extract, will require a much further and more detailed chemical investigation than we have so far been able to carry out ; in the next stage of our work we hope to be able to carry the matter further in this direction.

Attention may here be directed to the fact that all the four fractions of the original benzene extract were non-nitrogenous, or practically so, and that nothing at all corresponding with the nitrogenous humic-bodies always present in the extracts yielded by the bituminous and sub-bituminous coals examined could be found therein. The significance of this circumstance is reserved for further investigation.

G.—*Summary and Conclusions.*

The results of the investigations may be summarised as follows :—

(1) Benzene, when employed under the conditions described herein, has a considerable solvent action upon bituminous, sub-bituminous, and brown coals, extracting therefrom between 5 and 15 per cent. of the total coal substance.

(2) A large portion of the benzene extracts from the bituminous and sub-bituminous coals always comprise a group of nitrogenous "humic" bodies ; these are mainly responsible for the coking propensities of bituminous coals, in which they were found to be present to an extent of from 4·5 to 7·0 per cent.

of the whole coal substance. In the case of the non-caking or feebly caking sub-bituminous coals, they formed between 1 and 2 per cent. only of the coal substance; and in the case of the non-caking brown coal, they were not found at all in the benzene extract.

(3) The amount of "resins" ordinarily contained in bituminous coals does not exceed, and in most cases is considerably less than, 1 per cent. of the whole coal substance; and whilst such substances undoubtedly possess binding powers, they ordinarily contribute only in a minor degree to the coking propensities of the coals.

(4) The two non-caking semi-bituminous coals examined were acted upon by benzene to an extent of from 0·5 to 1·25 per cent. of their coal substances and their non-caking characters may be ascribed principally to the very small amounts of benzene-extractable "humic" bodies which they contained.

(5) In addition to the aforesaid nitrogenous "humic" bodies and non-nitrogenous "resins," all the benzene extracts of the bituminous and sub-bituminous coals contained important amounts of neutral wax-like non-nitrogenous bodies, of very low oxygen content, which do not contribute at all to their coking propensities.

(6) The residues left after the completion of the benzene extractions of the bituminous coals were *per se* all practically devoid of coking propensities; but their physical characters are probably not without some influence upon the actual coking process.

(7) The extract from the Morwell brown coal, which in total amount exceeded that of any of the other coals examined, was of quite a different character, consisting chiefly of non-nitrogenous unsaponifiable resenes, resene-esters and aliphatic or alicyclic acids (and esters), of which the two last named are highly oxygenated substances.

In conclusion, we desire to make due acknowledgment of the fact that the participation of two of us (A. R. Pearson and R. Quarendon) in the investigation has been made possible by personal grants from the Department of Scientific and Industrial Research, and that it is being continued with such aid.

Sulphur Studies in Coal Gas.—I. The Removal of Carbon Bisulphide by a Nickel Catalyst.

By E. V. Evans and H. Stanier.

Communicated by Dr. Henry E. Armstrong, F.R.S.—Received February 27, 1924.)

The use of nickel as a catalyst, together with hydrogen, has been studied during recent years in such minute detail that we are in a position to appreciate the part it plays and the precautions to be observed; among these, when the compound acted upon simply unites with hydrogen, the absence of sulphur is one of the chief conditions of success. In the Carpenter-Evans process* of removing the sulphur present as carbon bisulphide in coal gas, which has been in operation at works of the South Metropolitan Gas Company during several years past, the gas is passed over heated nickel spread out upon a neutral supporting material; the reduction of the sulphide takes place mainly in accordance with the equation $CS_2 + 2H_2 = C + 2H_2S$. Therefore, although the amount of the sulphur compounds in the gas is relatively small, the process is one in which sulphur, in a most active form, is always present. The primary object of our inquiry was to explain this apparently anomalous behaviour of the catalyst.

The temperature at which interaction takes place (420° C.) is considerably higher than that at which fatty oils, etc., are reduced by hydrogen; therefore, in presence of only a small proportion of hydrogen sulphide, the interaction $NiS + H_2 = Ni + H_2S$ might well proceed steadily from left to right, in presence of a large excess of hydrogen; in that case, a surface of metallic nickel would be constantly maintained. On trial, it was found that whether hydrogen containing a small proportion of hydrogen sulphide (20 to 30 grains per 100 cubic feet) be passed over *metallic nickel* or hydrogen alone over *nickel sulphide*, at 420° C., the concentration of the hydrogen sulphide in the outflowing gas is practically the same; in other words, an equilibrium is rapidly established at this temperature. The results of a series of such experiments are given in Table I. The amount of catalyst used was 0·1 gramme of nickel deposited upon 1·5 c.c. of pumice; the catalyst was heated at 420° C. and the gas passed over it at the rate of 0·5 cubic foot per hour. The apparatus used is shown in the figure, where *a* is the catalyst, *abc* the tube containing it (length *ab*, 5 inches, diameter half-inch), *c* rubber connection, *d* pear-shaped glass bead,

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* Carpenter, 'Trans. Inst. Gas Eng.' (1914) p. 183; Evans, 'J.S.C.I.,' vol. 34 (1915), p. 9.

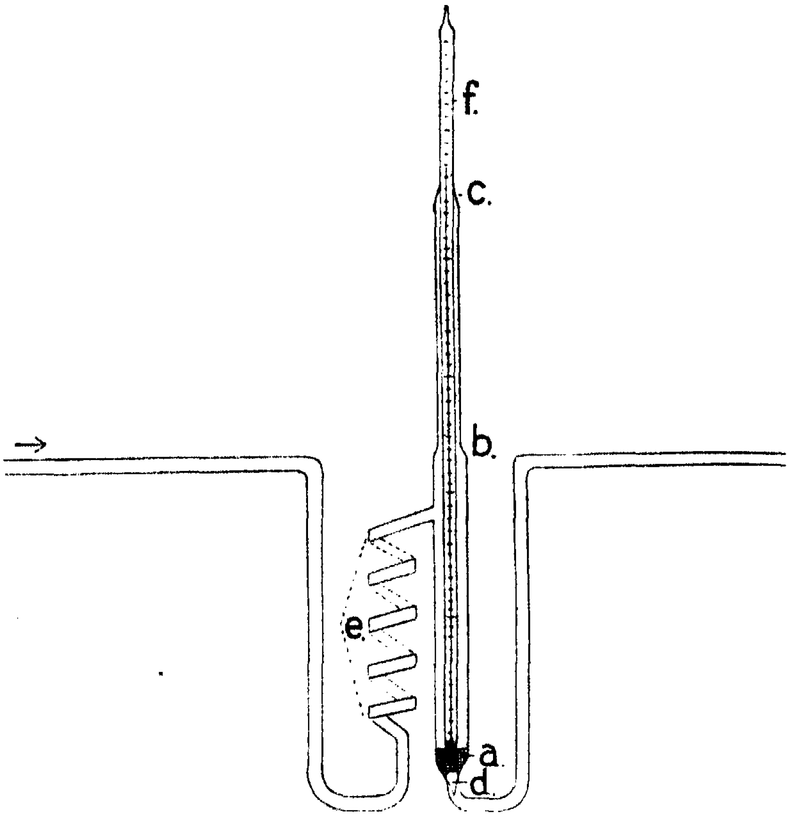

FIG. 1.—Catalyst tube.

Table I.

Test.	Concentrations of hydrogen sulphide in outflowing gas in six consecutive tests. Grains per 100 cubic feet.	
	(a) Hydrogen containing 24 grains hydrogen sulphide per 100 cubic feet over Ni catalyst.	(b) Hydrogen passed over sulphided catalyst.
1	6·0	4·8
2	6·1	4·7
3	6·2	5·0
4	6·2	5·1
5	5·8	5·0
6	5·8	5·0
Average	6·0 grains per 100 cubic feet.	4·9 grains per 100 cubic feet.

e preheating coil, *f* thermometer. The pumice particles used will pass through a sieve of 20 mesh to inch but not through one of 30 to inch.

Hydrogen containing hydrogen sulphide is, therefore, in equilibrium with the catalyst, at 420° C., when the concentration of the sulphide corresponds to 5–6 grains of sulphur per 100 cubic feet. The partial pressure of hydrogen in coal gas, however, is only about 0·5 atmospheres, so that at the equilibrium point the concentration of hydrogen sulphide is only half that in hydrogen alone, viz., 2·5 to 3·0 grains of sulphur per 100 cubic feet.

In reducing the carbon bisulphide in coal gas, 20 to 30 grains of hydrogen sulphide are produced per 100 cubic feet, which is an amount greatly in excess of the concentration in equilibrium at 420° C. Hence it is to be expected that the interaction $NiS + H_2 = Ni + H_2S$ will proceed to completion from right to left and nearly the whole of the nickel be ultimately converted into sulphide.

The gradual change of the catalyst into sulphide was very clearly indicated in an experiment in which only hydrogen and carbon bisulphide were used in proportions comparable with those in which these two gases are present in coal gas; the mixture was passed over the nickel catalyst at 420° C. The results are given in Table II.

Table II.—Hydrogen and CS_2 over nickel catalyst (0·1 gramme Ni on 1·5 c.c. pumice). Rate of gas—1 cubic foot per hour. Temperature—420° C.

Time from commencement.	Grains of sulphur per 100 cubic feet.			
	(*a*) initially as CS_2.	(*b*) after passing the catalyst.		
		(i) Total.	(ii) CS_2.	(iii) H_2S.
mins.				
0	—	—	—	—
20	26·0	6·3	—	5·93
50	23·8	6·8	0·37	6·43
85	27·0	9·7	—	9·3
105	24·0	12·0	0·4	11·8
125	24·0	14·75	0·45	14·3
142	24·0	16·4	—	15·95
155	24·5	19·6	—	19·15
175	24·5	20·0	0·46	19·54
190	25·0	23·0	0·42	22·58
200	25·0	24·0	—	23·6
215	25·0	24·5	0·44	24·1
230	24·5	25·0	—	24·6
200	26·0	26·0	—	25·6
270	24·25	24·0	—	23·6
280	24·25	24·0	—	23·6
290	25·0	24·5	0·4	24·1

During the first few hours the amount of sulphur in the gas which had passed the catalyst was much less than the amount originally present as bisulphide; presumably it is only when no metallic nickel remains exposed that sulphur is no longer removed. Nevertheless, the removal of the carbon bisulphide was effected with the same degree of completeness, even when sulphur no longer combined with the catalyst. We are, therefore, led to suppose that nickel sulphide must also be capable of acting catalytically in aiding the removal by hydrogen of the sulphur in carbon bisulphide.

That nickel sulphide can be substituted for metallic nickel as the catalyst has been proved by using the sulphide prepared by each of the following methods:—

(1) From hydrogen sulphide and nickel oxide obtained by igniting the nitrate.

(2) By precipitating with hydrogen sulphide a solution of a nickel salt containing an excess of sodium acetate.

Table III.—Catalyst—nickel sulphide (0·2 gramme Ni on 3 c.c. pumice). Rate of flow of coal gas—0·7 cubic foot per hour. Temperature—420° C.

Time from commencement.	Grains of sulphur per 100 cubic feet of gas.			
	(*a*) initially as CS_2 and organic S compounds.	(*b*) after passing the catalyst.		
		Total.	as CS_2 and organic S compounds.	as H_2S.
A. Nickel sulphide from Oxide.				
1 minute....	26	410	26·0	384·0
5 minutes	26	244	8·4	235·6
9 ,, ...	26	117	6·2	110·8
13 ,, ...	26	34	5·7	28·3
24 ,, ...	26	32	5·8	26·2
51 ,, ...	27·5	31	5·7	25·3
200 ,, ...	27	30	6·2	23·8
B. Nickel sulphide by precipitation.				
2 minutes	23	123	7·0	116·0
5 ,, ...	23	37	5·9	31·1
23 ,, ...	23	30	5·8	24·2
50 ,, ...	28	30·5	5·8	24·7
130 ,, ...	34·5	36	—	—

The activity of the sulphide was determined by passing coal gas over the heated substance at 420° C. The results are summarised in Table III (above).

The results when a nickel catalyst was used under similar conditions are given for the purpose of comparison.

Time from commencement.	Grains of sulphur per 100 cubic feet of gas.			
	(*a*) initially as CS_2 and organic compounds.	(*b*) after passing the catalyst.		
		Total.	as CS_2 and organic S compounds.	as H_2S.
O. Nickel by reduction of the chloride.				
10 minutes	40	7·3	5·5	1·8
15 "	40	7·3	—	—
25 "	40	8·0	5·3	2·7
45 "	40	9·0	5·6	3·4
56 "	40	10·0	—	—
73 "	40	20·0	—	—
83 "	40	34·0	—	—
87 "	39	36·0	—	—

A nickel sulphide catalyst, however obtained, is thus proved to be able to remove carbon bisulphide. It is to be noted that a considerable proportion of the sulphide is reduced during the first few minutes; in this period the catalyst is not so active as it is later on. Sulphur was found to be free in the sulphide obtained from the oxide, whereas that obtained by precipitation contained nickel and sulphur in the proportions required by the formula NiS; this difference accounts for the greater amount of sulphur evolved on the reduction of the sulphide from the oxide. As it has been shown that the conditions of equilibrium are such that, under the conditions observed, reduction to metallic nickel is not possible, it follows that a lower sulphide of nickel must be formed.

Bornmann,* by cryoscopically examining the melt obtained from nickel and sulphur, has definitely established the existence of a sub-sulphide, Ni_3S_2, which he has proved is the most stable sulphide of nickel at high temperatures. He was not able to obtain evidence of the existence of other sub-sulphides. The supposed lower sulphide, Ni_2S, according to him, is an eutectic mixture of nickel and Ni_3S_2.

The reduction of precipitated nickel sulphide by means of hydrogen has also been investigated; the results are given in Table IV. The gas was passed slowly over the sulphide supported on pumice.

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* 'Métallurgie,' vol. 5, p. 13 (1908).

Table IV.—Catalyst—nickel sulphide (0·3 gramme NiS on 3 c.c. pumice). Rate of flow of H_2, 0·5 cubic feet per hour. Temperature, 420° C.

Time from commencement.	Grains S per 100 cubic feet in outflowing gas.
2 minutes	124·0
5 „	54·6
8 „	14·9
24 „	3·3
40 „	3·1
45 „	2·5
55 „	2·5
68 „	2·7

Reduction took place at first very rapidly; it quickly fell to a constant rate, corresponding approximately to the rate of reduction to metallic nickel (*see* Table I). This period of rapid reduction appears to be that during which the lower metallic sulphide is formed; an analysis of the product after the rate of reduction had become slow and constant showed the composition to be as indicated below. (The results given are from four different experiments.)

Ni : S = 73·2 : 26·8
72·9 : 27·1
72·06 : 27·94
73·63 : 26·37
Ni_3S_2 requires Ni : S = 73·3 : 26·7

Thus it seems that nickel sulphide is primarily reduced to Bornmann's sub-sulphide, Ni_3S_2; this sulphide, under suitable conditions, is ultimately, though only very slowly, reduced to metallic nickel. The equilibrium conditions indicated by the results in Table I refer, therefore, to the interaction $Ni_3S_2 + 2H_2 = 2H_2S + 3Ni$, and Ni_3S_2 may be regarded as the compound which ultimately becomes the catalyst, whether nickel or the normal sulphide (NiS) be taken as the initial agent.

FUNCTION OF NICKEL SUB-SULPHIDE AS CATALYST.

The peculiar action exercised by a sub-sulphide of nickel as a catalyst in promoting the reduction of carbon bisulphide is of considerable interest.

In other hydrogenating processes—the hydrogenation of phenols, carbon monoxide and dioxide, unsaturated oils, etc.—the sub-sulphide has no catalytic activity; in fact, sulphur is a very active poison of nickel. Recently, however, towards the conclusion of this work, our attention was drawn to a similar case in which the sulphide has been found to act as a catalyst, viz., in the reduction by hydrogen of sulphur dioxide.* It is interesting to note that, in both these cases, the compounds affected are sulphur compounds for which the sub-sulphide of nickel might be expected to have some affinity.

In view of the readiness with which carbon bisulphide is converted into thiocarbonate, it is more than probable that it enters initially into combination with the nickel sub-sulphide, and it is conceivable that a compound is formed which is then broken down into nickel sulphide and "carbon."

On the other hand, it is necessary to take into account the exothermic nature of carbon bisulphide and the peculiar instability of the carbon monosulphide discovered and studied by Dewar and Jones. It is now commonly assumed that the catalyst acts by entering into association with the compounds whose interaction it promotes; applying this view to carbon bisulphide and hydrogen, various possibilities are to be considered, although in view of our ignorance of the structure of the metallic sub-sulphide, it is impossible to define the nature of the compound formed with any degree of probability. It may be suggested, for example, that whilst one of the two sulphur atoms of the bisulphide combines with the sub-sulphide, the other combines momentarily with two hydrogen atoms, forming a compound which breaks down into hydrogen sulphide and carbon monosulphide. This monosulphide may at once undergo reduction to a hydride, several molecules of which then interact, giving rise to the complex molecule of "carbon" and hydrogen sulphide, or further reduction may take place to methane. Carbon dioxide and monoxide, it is well known, are entirely reduced to methane.

That nickel sub-sulphide and carbon bisulphide give rise to the normal sulphide has been proved experimentally by passing nitrogen containing the bisulphide over the sub-sulphide at 420° C. About 0·3 gramme of Ni_3S_2 on pumice was used and the gas, containing 270 grains of sulphur (as carbon bisulphide) per 100 cubic feet, was passed at the rate of 0·5 cubic feet per hour. The outflowing gas, even five minutes after the commencement of the experiment, contained but 70 grains of sulphur per 100 cubic feet, 200 grains per 100 cubic feet having been removed, therefore, by the sub-sulphide. By determining the rate at which it was reduced in hydrogen the latter was found to have been converted into the normal sulphide.

* Tomkinson, 'C.R.,' vol. 176, pp. 35–36 (1923).

It will be shown later that the velocity of the interaction of hydrogen and carbon bisulphide is governed by the rate of reduction of the nickel sulphide present, thus affording striking support for the conclusion that the sulphide is one of the products of change.

VELOCITY OF INTERACTION.

(a) *Comparison of* Ni, Ni_3S_2, *and* NiS *as Initial Agents.*

Equivalent quantities of the three substances were deposited on equal weights of pumice and coal gas was passed over each catalyst at 420° C. The maximum speed consistent with reduction of the sulphur in the gas—after removing hydrogen sulphide—to a definite concentration, viz., 8 grains per 100 cubic feet, was determined at frequent intervals; the rate of flow of the gas, throughout the test, was varied so as to conform as nearly as possible to this maximum at any given moment. The results are clearly expressed by the curves (fig. 2) given below, obtained by plotting the maximum rates of change corresponding to the passage of different volumes of gas. To obtain uniformity, the catalysts were all prepared from nickel oxide. A sufficient quantity of pumice was soaked in a concentrated solution of the nitrate, then dried and ignited; the amount equivalent to 0·05 gramme nickel (about 0·75 c.c.) was either reduced or sulphided or sulphided and reduced, according as either the metal, the sulphide or the sub-sulphide was required.

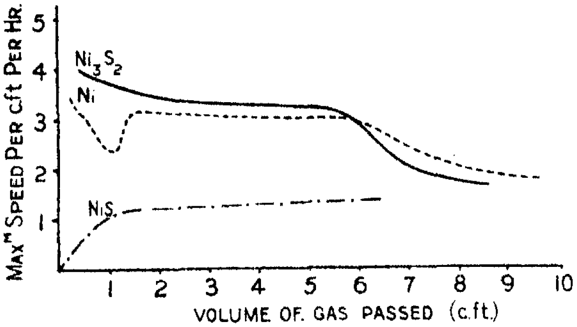


FIG. 2.—Velocity Curves for Ni, Ni_3S_2 and NiS.

From the curves it can be seen that the nickel sub-sulphide has the greatest activity, although that of the nickel is very little less. Nickel sulphide (normal), as already indicated in previous experiments, is almost inactive initially and although at first its activity rapidly increases, it long remains far less active than either Ni_3S_2 or Ni. It is noteworthy, however, that the activity of both these agents gradually falls and ultimately approaches that of the normal sulphide, which remains fairly constant after the initial period.

If these facts be considered in the light of the explanation which has been put forward, their meaning becomes obvious. Commencing with nickel as the catalyst, the metal present in the surface layers will rapidly take up sulphur from the gas and be converted into the sub-sulphide ; this latter in its turn will also remove sulphur from the gas, being converted into normal sulphide. The velocity of the interaction, which is a function of the amount of Ni_3S_2 with which the gas comes into contact, will therefore decrease as the action proceeds and the amount of the sub-sulphide decreases. The latter, however, is being continually regenerated by the reduction of the normal sulphide which is formed and equilibrium will be established when the rate of conversion of sub-sulphide into normal sulphide is equal to the rate of regeneration. At this point the velocity of the action should become practically constant and equal to the rate of reduction of the normal sulphide present, any decrease being due only to the deposition of carbon. The same conditions should ultimately be attained, starting either from the sub-sulphide or from normal sulphide.

It was noted that in a number of experiments in which the rate of flow of the gas differed considerably from the maximum speed, especially when the rate had been allowed to fall too quickly, the activity of the catalyst was renewed. This also happened when the cold catalyst was left overnight in contact with coal-gas and the experiment continued the following morning. This increased activity is probably due to changes taking place within the mass of the catalyst. When the action takes place at high speeds, the gases have not time to diffuse throughout the whole mass, so that a core of the original material is left within. Some interaction may be slowly taking place, between this core and the surrounding layers, which only becomes evident when the even flow of the gas is interrupted.

(b) *Action of Promoters.*

It is known that in the case of many catalytic processes the activity of the catalyst may be considerably increased by associating it with certain substances known as "promoters." These are usually infusible and difficultly reducible oxides, a long list of which is given in the several Badische patents.* Experiments have been made to test the effect of various oxides on the activity of the nickel in reducing carbon bisulphide. It has been found that the speed is increased to the greatest extent by the oxides of thorium, aluminium, chromium

* Badische E.P. 2306/14. U.S.P. 1,068,968/13. D.R.P. 279, 582.

and beryllium. The maximum speeds obtainable through the intervention of these four oxides compared with that of nickel alone are given in the following table. As before, the maximum speed is taken as that at which the gas may be passed over the catalyst to reduce the sulphur content to 8 grains per 100 cubic feet.

Table V.—Catalyst—0·1 gramme Ni deposited on pumice, together with promoter. Temperature, 400° C.

Promoter.	Optimum concentration of promoter as percentage of nickel used.	Maximum speed, cubic feet per hour.
None (nickel only)	—	3·2
Thoria	20—30 per cent.	9·0
Alumina	10 per cent.	7·2
Chromium oxide	15 per cent.	7·2
Beryllium oxide	—	6·4

The maximum increase in activity is effected by thoria, which increases the speed of action by about 200 per cent. Whether the oxides have a specific effect or act merely by extending the subdivision of the catalyst, we have yet to ascertain.

(*c*) *Influence of Temperature.*

The effect of temperature on the velocity of interaction was next studied. As it was essential that comparisons of the velocities at different temperatures should be made only after equilibrium had been established at the surface of the catalyst, nickel sulphide was used as the initial material, as the final equilibrium is more quickly attained by using this material than if either nickel or the sub-sulphide be taken. The coal-gas was passed at a constant velocity over the catalyst and the amount of the bisulphide removed was determined at several temperatures. The velocity of the hydrogenation at a constant rate of flow is proportional to the number of grains of bisulphide removed per 100 cubic feet, so that the latter quantity plotted against the temperature gives a true velocity-temperature curve. A second series of experiments was carried out with nickel sulphide associated with thoria. The results are given in Table VI.

Table VI.—Rate of flow of gas over catalyst 4·0 cubic feet per hour.

Catalysts used :—

(1) Nickel sulphide obtained from nickel oxide by exposure to hydrogen sulphide at 200° C. during two hours—0·05 gramme Ni on 0·75 c.c. pumice.

(2) Nickel sulphide similarly obtained from mixed oxides of nickel and thorium. $ThO_2 = 20$ per cent. weight of the nickel (0·05 gramme).

In each experiment, several determinations were made at each temperature and the mean only of these is given in the table ; two experiments (*a* and *b*) were carried out with each catalyst.

(1) Nickel Sulphide only.

Temperature °C.		CS_2 and organic sulphur compounds as grains sulphur per 100 cubic feet of gas.			
		(1) before passing catalyst.	(2) after passing catalyst.	(3) removed by catalyst.	Mean.
330	*a*	43	38·4	4·6	5·05
	b	32·8	27·3	5·5	
350	*a*	43	36·8	6·2	7·25
	b	32·8	24·5	8·3	
385	*a*	43	30·5	12·5	13·25
	b	32·8	18·8	14·0	
400	*b*	32·8	14·5	—	18·3
420	*a*	43	19·6	23·4	23·0
	b	32·8	10·2	22·6	

(2) Nickel Sulphide-thoria.

Temperature °C.		CS_2 and organic sulphur compounds as grains sulphur per 100 cubic feet of gas.			
		(1) before passing catalyst.	(2) after passing catalyst.	(3) removed by catalyst.	Mean.
300	*a*	27	22·3	4·7	4·7
	b	27	22·3	4·7	
328	*a*	27	17·0		10·0
334	*b*	27	16·4		10·6
358	*a*	27	11·2		15·8
366	*b*	33	15·0		18·0
378	*a*	30	8·5		21·5

The curves (fig. 3) given below have been plotted from these results.

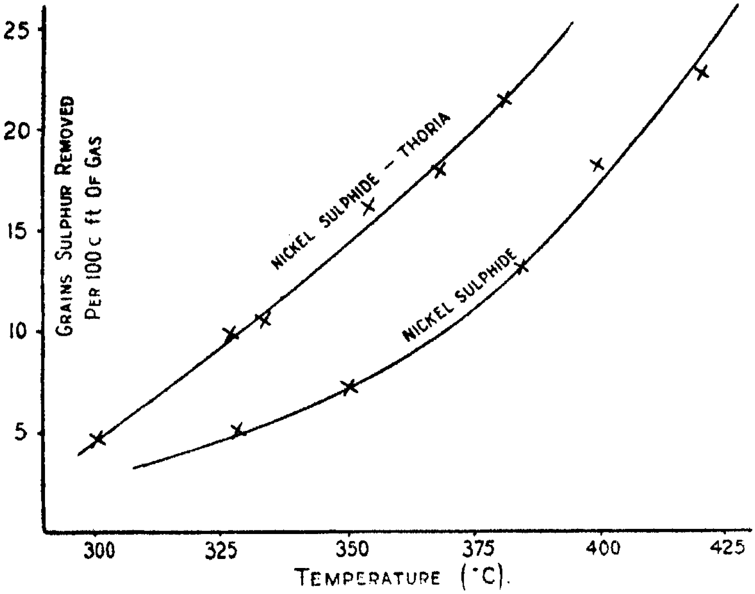


Fig. 3.—Velocity—Temperature Curves. Rate of flow of gas over catalyst—4 cubic feet per hour.

The temperature coefficient of nickel sulphide is thus about 1·2 for every 10° C. rise and is fairly constant at temperatures between 300° and 400° C.; that of the nickel sulphide-thoria, however, gradually decreases from about 1·35 at 300° C. to 1·2 at 350° C. and 1·14 at 370° C. This indicates that the thoria mixture has maximum activity relatively to that of nickel sulphide about 350° C. At this temperature, the speed of the reduction is about doubled, but, as the temperature is raised, the percentage increase due to the thoria slowly falls. At a given speed of change, the nickel sulphide-thoria can be used at a temperature about 40° C. lower than nickel sulphide.

(*d*) *Influence of rate of flow of gas on the Velocity of Interaction.*

In the early experiments it was noticed that the velocity was considerably affected by the rate of flow of gas over the catalyst. A few results are given in Table VII which show the variation when gas is passed over a particular weight of nickel sulphide at one particular temperature but at different speeds.

The velocity of interaction is raised as the rate of flow over the catalyst is increased. This is possibly explained by the formation at low speeds of a film of the products on the catalyst, tending to delay contact with the acting gases and so reduce the speed of interaction.

Table VII.—Catalyst—Nickel sulphide (0·05 gramme Ni) on 0·75 c.c. pumice. Temperature—350° C.

Rate of flow of gas, cubic feet per hour.	Grains sulphur per 100 cubic feet gas as CS_2.			Milligrains of S as CS_2 converted per hour.
	(*a*) initially.	(*b*) finally.	(*c*) converted by catalyst.	
0·39	32·5	9·0	23·5	91·5
0·61	33·0	8·0	25·0	152·5
1·06	33·0	17·0	16·0	169·5
2·00	27·5	28·2	9·3	186·0
4·00	—	—	7·2	288·0

(*e*) *Relationship between the Velocity of Interaction and the rate of reduction of the Nickel Sulphide.*

In accordance with the explanation which has been advanced, when equilibrium is attained at the surface of the catalyst, the velocity of the interaction should be measured by that of the reduction of the normal sulphide present; this latter is difficult to determine with any degree of accuracy for several reasons :—

(1) The rate of reduction is not constant but gradually decreases as the amount of normal sulphide diminishes.

(2) It must necessarily be determined at the same rate of gas-flow as the velocity of the action. Therefore a small quantity only of the catalyst can be used, as in order to determine the velocity of the action the rate of flow must be such that the removal of carbon bisulphide is incomplete. Large quantities of catalyst merely involve the use of very high gas speeds and consequent difficulty in controlling temperature and preheating.

(3) The use of a small quantity of catalyst involves the estimation of very minute quantities of hydrogen sulphide, entailing inaccuracies in titration, etc.

The method adopted was to use a small quantity of nickel sulphide catalyst over which the rate of change had been determined at a definite speed of gas, the gas being passed during several hours in order to set up equilibrium conditions in the surface of the catalyst. Coal-gas, freed from bisulphide vapour, was then passed over at the same temperature and rate of flow, and the sulphur removed determined during short intervals of time by absorption in normal soda and estimation of the sodium sulphide by standard iodine and thiosulphate, in the usual way. The apparatus was so arranged that the outflowing gas could be passed through any one of several washers containing the caustic soda solution without interrupting the experiment.

The maximum rates of reduction were deduced from curves obtained by plotting the quantity of sulphur removed as hydrogen sulphide against time.

A comparison was also made between a nickel sulphide and a nickel sulphide-thoria catalyst. The results are given below.

Table VIII.—(*a*) Catalyst—Nickel sulphide (0·05 gramme Ni) on 0·75 c.c. pumice.

Temperature °C.	Rate of flow of gas. cubic feet per hour.	Velocity of CS_2 removal, milligrains S per hour.	Maximum rate of reduction of sulphide present, milligrains S per hour.
350	0·39	91·5	80
350	0·61	152·5	130
350	1·06	169·5	130
385	1·04	239·0	300

(*b*) Catalysts (1) nickel sulphide (0·025 gramme Ni) on 0·37 c.c. pumice; (2) nickel sulphide (0·025 gramme Ni) + thoria. ($ThO_2 \equiv 20$ per cent. of the nickel by weight.) Temperature, 350° C. Rate of flow of gas, 1 cubic foot per hour.

Catalyst.	Velocity of CS_2 removal, milligrains S per hour	Maximum rate of reduction of sulphide present, milligrains S per hour.
Nickel sulphide	93	77
Nickel sulphide-thoria	138	118

The curves (fig. 4) showing the rates of reduction by these last two catalysts are given here and will serve to show how the maximum rates have been deduced.

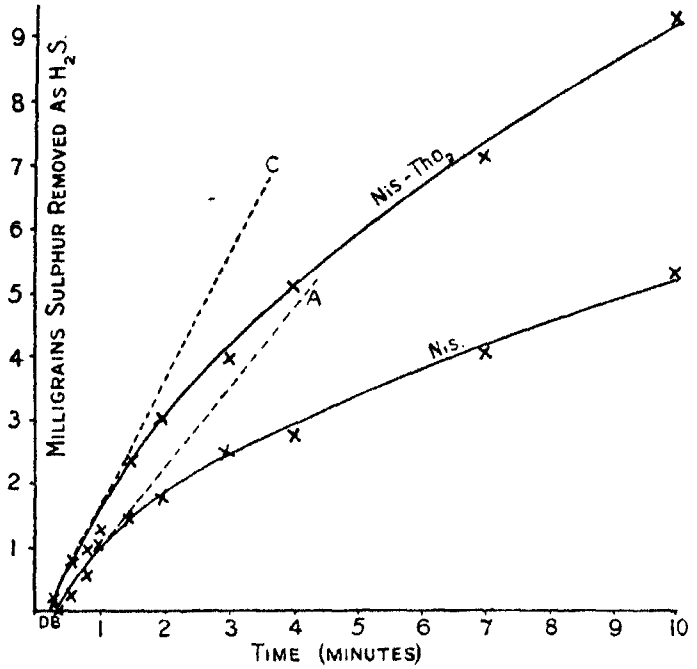
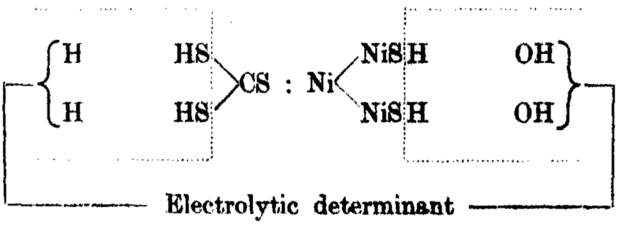


FIG. 4.

The maximum rates of reduction, expressed as milligrains of sulphur removed per minute, are given by the tangents of the angles made by the lines AB and CD with the horizontal axis.

Taking into consideration the minute quantities of hydrogen sulphide which are estimated, and the consequent large experimental error, these results indicate a fair measure of agreement between the rate of the hydrogenation and the rate of the reduction of the nickel sulphide when equilibrium is established. It will also be observed that the rate of reduction of the sulphide is increased by thoria in about the same ratio as is the velocity of the hydrogenation.

Professor Armstrong points out to us that, assuming that the action take place in a complex circuit, a possible picture of the initial process is given in the following tentative scheme :—



$$\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right. \qquad \begin{matrix}\mathrm{HS}\\\mathrm{HS}\end{matrix}\!\!>\!\mathrm{CS} : \mathrm{Ni}\!<\!\begin{matrix}\mathrm{NiS\,H}\\\mathrm{NiS\,H}\end{matrix} \qquad \left.\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}\right\}$$

The dotted lines show the manner in which sulphur might be separated and the catalyst regenerated.

The authors desire to thank the President, Dr. Charles Carpenter, and the Directors of the South Metropolitan Gas Company, for permission to publish this paper; and also Miss E. M. Sheldon and Mr. S. Medsforth for their assistance with the experimental work.

Half-Integral Quantum Numbers in the Theory of the Stark Effect and a General Hypothesis of Fractional Quantum Numbers.[*]

By A. M. MOSHARRAFA, Ph.D., D.Sc.

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§ 1. Indications of the occurrence of fractional quantum numbers have already been found by Kratzer[†] from a study of certain band spectra, and by Curtis[‡] in his experimental investigation of helium bands. Heisenberg[§] has also employed half-integral numbers in a quantum theory of the anomalous Zeeman effect with considerable success. The fourth of the slightly extended quantum conditions recently suggested by W. Wilson[||] and applied by the present writer[¶] to the Zeeman effect involves a fractional quantum number, as O. W. Richardson[**] has pointed out.

K. F. Niessen,[††] in his work on the positively ionised hydrogen molecule, observes certain discontinuities in the energy graphs between symmetrical and asymmetrical models which strongly suggest the occurrence of half-integral quantum orbits for the latter. He refrains, however, from making this assumption, on the ground that it would necessitate the adoption of half numbers in the somewhat allied case of the Stark effect.

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[*] This paper summarises one portion of a Thesis approved for D.Sc. degree in the University of London.

[†] 'Sitz. d. Bayer. Akad.,' p. 107 (March, 1922).

[‡] 'Roy. Soc. Proc.,' A, vol. 103, p. 321 (1923).

[§] 'Zeitschr. f. Phys.,' vol. 8, p. 273 (1921–22).

[||] 'Roy. Soc. Proc.,' A, vol. 102, p. 478 (1922).

[¶] 'Roy. Soc. Proc.,' A, vol. 102, p. 529 (1923).

[**] 'Phil. Mag.,' vol. 46, p. 911 (1923).

[††] "Zur Quantentheorie des Wasserstoffmolekülions" (J. Van Druten, Utrecht), p. 108 (1922).

The aim of this paper is to draw attention to certain experimental and theoretical indications of the occurrence of half-integral numbers in the Stark effect and to the special merit of a general quantum hypothesis involving fractional numbers.

§ 2. From the point of view of the quantum theory, the choice of the particular set of Hamiltonian co-ordinates for a degenerate system (in the Schwarzschild sense) affects, as is well known, the orbital configurations determined. Hence, some criterion is necessary to determine the choice. Sommerfeld* maintains that the "proper" set is the one in which the variables are separate when the relativity change in mass is taken into account. If such a unique set is available, then a definite physical picture of the steady states of the system could be ascertained, otherwise the physical orbital configurations are indeterminable.

Consider now a system of particles which possesses a unique set of proper co-ordinates (p, q), and, consequently, a corresponding determinable ensemble of physical orbits $\Gamma_p{}^i$, under certain conditions, but *no* proper co-ordinates, in the Sommerfeld sense, under slightly altered conditions: as in the case of the Stark effect. If under the latter conditions the variables are separable on non-relativistic dynamics in the co-ordinates (P, Q), then only a portion of the total number of orbits $\Gamma_P{}^i$ determined on (P, Q) will in general be such as to coincide with members of the ensemble $\Gamma_p{}^i$ when the difference in conditions vanishes. Consequently, only this portion of orbits can be said to possess a physical reality. We shall, however, show that, in the case of the Stark effect, it is possible by adopting half-integral quantum numbers to increase the number of orbits among $\Gamma_P{}^i$ which so possess a physical reality: in fact, to multiply it by 2. Moreover, it will be shown that the totality of coincident physical orbits thus obtained will be such as to comprise *all* the orbits for which the geometrical conditions allow of (P, Q), as well as (p, q) as proper co-ordinates.

We identify the system considered in the last paragraph with the hydrogen atom in the absence and presence of an external electric field F respectively. Here the Hamiltonian co-ordinates in the spherical polar system (r, θ, ψ) are the proper co-ordinates (denoted by p, q above) in the absence of the field; whereas no proper co-ordinates are available in the presence of the field. In the parabolic system (ξ, η, ψ), however, the Hamiltonian co-ordinates (denoted by P, Q above) are separable on non-relativistic dynamics. The ensemble of physical orbits $\Gamma_p{}^i$ defined in the absence of the field are given, on neglecting the relativity refinement, by the equations

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* 'Atombau und Spectrallinien,' English translation, p. 571 (1923).

$$\left.\begin{aligned} dt &= \frac{m_0 dr}{\sqrt{\alpha_1 + 2m_0 e\mathrm{E}/r - \alpha_2/r^2}} \\ 0 &= \frac{-dr}{r^2\sqrt{\alpha_1 + 2m_0 e\mathrm{E}/r - \alpha_2/r^2}} + \frac{d\theta}{\sqrt{\alpha_2 - \alpha_3/\sin^2\theta}} \\ 0 &= \frac{-d\theta}{\sin^2\theta\sqrt{\alpha_2 - \alpha_3/\sin^2\theta}} + \frac{d\psi}{\sqrt{\alpha_3}} \end{aligned}\right\} \qquad (1)$$

where m_0 is the mass of the electron, $(-e)$ and E the respective charges on the electron and nucleus, and

$$\alpha_1 = 2m_0\mathrm{W}, \qquad (2)$$

W being the total energy.

The constants α_1, α_2, α_3 are defined by the quantum conditions :—

$$\left.\begin{aligned} \mathrm{J}_r &= \int_0 \sqrt{\alpha_1 + 2m_0 e\mathrm{E}/r - \alpha_2/r^2}\ dr = n_r h \\ \mathrm{J}_\theta &= \int_0 \sqrt{\alpha_2 - \alpha_3/\sin^2\theta}\ d\theta = n_\theta h \\ \mathrm{J}_\psi &= \int_0^{2\pi} \sqrt{\alpha_3}\, d\psi = n^\psi h \end{aligned}\right\} \qquad (3)$$

On the parabolic system (ξ, η, ψ) if the field is assumed to vanish, we have, on the other hand, for the ensemble $\Gamma_{\mathrm{P}}{}^i$ the equations :—

$$\left.\begin{aligned} dt &= \frac{m_0\xi^2\, d\xi}{\sqrt{\alpha_1\xi^2 + 2m_0 e\mathrm{E} + \alpha_2' - \alpha_3/\xi^2}} + \frac{m_0\eta^2\, d\eta}{\sqrt{\alpha_1\eta^2 + 2m_0 e\mathrm{E} - \alpha_2' - \alpha_3/\eta^2}} \\ 0 &= \frac{d\xi}{\sqrt{\alpha_1\xi^2 + 2m_0 e\mathrm{E} + \alpha_2' - \alpha_3/\xi^2}} - \frac{d\eta}{\sqrt{\alpha_1\eta^2 + 2m_0 e\mathrm{E} - \alpha_2' - \alpha_3/\eta^2}} \\ 0 &= \frac{-d\xi}{\xi^2\sqrt{\alpha_1\xi^2 + 2m_0 e\mathrm{E} + \alpha_2' - \alpha_3/\xi^2}} \\ &\qquad + \frac{d\eta}{\eta^2\sqrt{\alpha_1\eta^2 + 2m_0 e\mathrm{E} - \alpha_2' - \alpha_3/\eta^2}} + \frac{d\psi}{\sqrt{\alpha_3}} \end{aligned}\right\}, \qquad (4)$$

where α_1, α_2', α_3 are defined by

$$\left.\begin{aligned} \mathrm{J}_\xi &= \int_0 \sqrt{\alpha_1\xi^2 + 2m_0 e\mathrm{E} + \alpha_2' - \alpha_3/\xi^2}\ d\xi = n_\xi h \\ \mathrm{J}_\eta &= \int_0 \sqrt{\alpha_1\eta^2 + 2m_0 e\mathrm{E} - \alpha_2' - \alpha_3/\eta^2}\ d\eta = n_\eta h \\ \mathrm{J}_\psi &= \int_0^{2\pi} \sqrt{\alpha_3}\, d\psi = n_\psi h \end{aligned}\right\}. \qquad (5)$$

The values of α_1 and α_3 are identical on the two systems of co-ordinates (which we have anticipated in the notation), giving:

$$\left.\begin{aligned} \alpha_1 &= -\left(\frac{2\pi m_0 e\mathrm{E}}{\mathrm{J}_r + \mathrm{J}_\theta + \mathrm{J}_\psi}\right)^2 = -\left(\frac{2\pi m_0 e\mathrm{E}}{\mathrm{J}_\xi + \mathrm{J}_\eta + \mathrm{J}_\psi}\right)^2 \\ \alpha_3 &= (\mathrm{J}_\psi/2\pi)^2 \end{aligned}\right\}, \tag{6}$$

provided

$$n_r + n_\theta = n_\xi + n_\eta, \tag{7}$$

and n_ψ is the same, for the two corresponding orbits considered. Further, the constants α_2, α_2' are given by

$$\alpha_2 = (\mathrm{J}_\theta + \mathrm{J}_\psi)^2/(2\pi)^2, \tag{8}$$

$$\left.\begin{aligned} \alpha_2' &= (\partial\mathrm{S}/\partial\xi)^2 - 2m_0\xi^2\mathrm{W} - 2m_0 e\mathrm{E} + \mathrm{J}_\psi^2/(2\pi)^2\,\xi^2 \\ &= -(\partial\mathrm{S}/\partial\eta)^2 + 2m_0\eta^2\mathrm{W} + 2m_0 e\mathrm{E} - \mathrm{J}_\psi^2/(2\pi)^2\,\eta^2 \\ &= 2m_0 e\mathrm{E}\,(\mathrm{J}_\xi - \mathrm{J}_\eta)/(\mathrm{J}_\xi + \mathrm{J}_\eta + \mathrm{J}_\psi) \end{aligned}\right\}, \tag{9}$$

where S is the function of action. For the relation between the co-ordinates themselves we have

$$\left.\begin{aligned} \xi &= \sqrt{2r}\cos\theta/2\,; \quad r = \tfrac{1}{2}(\xi^2 + \eta^2) \\ \eta &= \sqrt{2r}\sin\theta/2\,; \quad \theta = 2\tan^{-1}(\eta/\xi) \end{aligned}\right\} \tag{10}$$

From (3), (5), (6) and (8) it follows that

$$\left.\begin{aligned} 2\mathrm{J}_\xi &= \mathrm{J}_r + \mathrm{J}_\theta + \pi\alpha_2'/\sqrt{-\alpha_1} \\ 2\mathrm{J}_\eta &= \mathrm{J}_r + \mathrm{J}_\theta - \pi\alpha_2'/\sqrt{-\alpha_1} \end{aligned}\right\} \tag{11}$$

and from (9):

$$\alpha_2' = \tfrac{1}{2}\left[\left(\frac{\partial\mathrm{S}}{\partial\xi}\right)^2 - \left(\frac{\partial\mathrm{S}}{\partial\eta}\right)^2\right] - m_0\mathrm{W}(\xi^2 - \eta^2) + \tfrac{1}{2}\left(\frac{\mathrm{J}\psi}{2\pi}\right)^2\left(\frac{1}{\xi^2} - \frac{1}{\eta^2}\right), \tag{12}$$

so that on substituting in this last equation from (10) and on using

$$\begin{aligned} \partial\mathrm{S}/\partial\xi &= \frac{\partial\mathrm{S}}{\partial r}\cdot\frac{\partial r}{\partial\xi} + \frac{\partial\mathrm{S}}{\partial\theta}\cdot\frac{\partial\theta}{\partial\xi} \\ &= \sqrt{2r}\cos\theta/2\,\frac{\partial\mathrm{S}}{\partial r} - \sqrt{\frac{2}{r}}\sin\theta/2\,\frac{\partial\mathrm{S}}{\partial\theta} \\ \partial\mathrm{S}/\partial\eta &= \frac{\partial\mathrm{S}}{\partial r}\frac{\partial r}{\partial\eta} + \frac{\partial\mathrm{S}}{\partial\theta}\frac{\partial\theta}{\partial\eta} \\ &= \sqrt{2r}\sin\theta/2\,\frac{\partial\mathrm{S}}{\partial r} + \sqrt{\frac{2}{r}}\cos\theta/2\,\frac{\partial\mathrm{S}}{\partial\theta} \end{aligned}$$

we have

$$\alpha_2' = r\cos\theta\left[\left(\frac{\partial S}{\partial r}\right)^2 - 2m_0W - \left(\frac{n_\psi h}{2\pi}\right)^2 \Big/ r^2\sin^2\theta\right] - 2\sin\theta\,\frac{\partial S}{\partial r}\,\frac{\partial S}{\partial\theta} - \frac{\cos\theta}{r}\left(\frac{\partial S}{\partial\theta}\right)^2$$

$$= -2\sin\theta\frac{\partial S}{\partial r}\,\frac{\partial S}{\partial\theta} + 2m_0eE\cos\theta - \frac{2\cos\theta}{r}\left(\frac{\partial S}{\partial\theta}\right)^2 - \frac{2\cos\theta}{r\sin^2\theta}\left(\frac{n_\psi h}{2\pi}\right)^2 \qquad (13)$$

since

$$(\partial S/\partial r)^2 - 2m_0W = \frac{2m_0eE}{r} - \frac{1}{r^2}\left(\frac{\partial S}{\partial\theta}\right)^2 \frac{1}{r^2\sin^2\theta}\left(\frac{n_\psi h}{2\pi}\right)^2.$$

As α_2' is constant throughout the motion, we obtain its value from (13) on putting $\partial S/\partial\theta = 0$, thus

$$\alpha_2' = 2m_0eE\cos\beta - \frac{2}{r_0}\,\frac{\cos\beta}{\sin^2\beta}\left(\frac{n_\psi h}{2\pi}\right)^2 \qquad (14)$$

where β is the root of

$$\partial S/\partial\theta = \sqrt{[(J_\theta + J_\psi)^2/(2\pi)^2 - J_\psi^2/(2\pi\sin\theta)^2]} = 0$$

so that

$$\sin\beta = \pm J_\psi/(J_\theta + J_\psi)$$

and r_0 is the value of r at $\theta = \beta$.

And on substituting for β in (14) we get

$$\alpha_2' = \pm 2m_0eE\sqrt{[1 - J_\psi^2/(J_\theta + J_\psi)^2]} \times [1 - (J_\theta + J_\psi)^2/(2\pi)^2 m_0eEr_0] \qquad (15)$$

(11) and (15) yield

$$\left.\begin{aligned} 2J_\xi &= J_r + J_\theta \pm (J_r + J_\theta + J_\psi)\left[1 - \frac{(J_\theta + J_\psi)^2}{(2\pi)^2 m_0eEr_0}\right]\sqrt{[1 - J_\psi^2/(J_\theta + J_\psi)^2]} \\ 2J_\eta &= J_r + J_\theta \mp (J_r + J_\theta + J_\psi)\left[1 - \frac{(J_\theta + J_\psi)^2}{(2\pi)^2 m_0eEr_0}\right]\sqrt{[1 - J_\psi^2/(J_\theta + J_\psi)^2]} \end{aligned}\right\} \qquad (16)$$

(16) shows that if J_r, J_θ, J_ψ are integral multiples of h, then J_ξ, J_η will not in general be so for any given orbit. Consequently the two sets of orbits, Γ_p^i, Γ_P^i defined by equations [(1) + (3)] and [(4) + (5)] respectively, where n_r, n_θ, n_ψ, n_ξ, n_η are all assumed to be integers, are not identical. Consider, however, the class of orbits $\Gamma_{p,P}^i$ which satisfy one or both of the two conditions :

$$1 - J_\psi^2/(J_\theta + J_\psi)^2 = 0, \qquad (17)$$

$$1 - (J_\theta + J_\psi)^2/(2\pi)^2 m_0eEr = 0. \qquad (18)$$

We have from (16) for this class of orbits

$$\left.\begin{aligned} 2J_\xi &= J_r + J_\theta \\ 2J_\eta &= J_r + J_\theta \end{aligned}\right\}, \qquad (19)$$

so that one-half of this class, viz. those orbits for which $(n_r + n_\theta)$ is even,* is common between $\Gamma_\nu{}^i$ and $\Gamma_{\mathrm{P}}{}^i$ if all quantum numbers are assumed to be integers.

We next examine the geometrical meaning of the two conditions (17) and (18). From (17) we have

$$J_\theta = 0, \tag{20}$$

in other words, the orbits lie in the equatorial plane or else are merely straight line orbits. From (18) we have

$$\left.\begin{aligned} r &= (J_\theta + J_\psi)^2/(2\pi)^2 m_0 e\mathrm{E} \\ &= \text{constant} \end{aligned}\right\}, \tag{21}$$

in other words, the orbit is a circle† and

$$J_r = 0. \tag{22}$$

Hence for the class of orbits $\Gamma_{\nu,\mathrm{P}}{}^i$ at least one of the two co-ordinates (r, θ) is constant, and consequently *the variables are separable for such orbits in either of the two systems of co-ordinates on relativistic mechanics.* We should, therefore, expect either system to furnish us with the unique physical picture of these orbits. It is seen from (19) that if we write

$$n_\xi = m/2 = n_\eta \tag{23}$$

for these paths, where m is an integer $(= \overline{n_r + n_\theta})$, this agreement between the two systems is effected. The orbits defined by (4) and (5) will now have in common with those defined by (1) and (3) exactly those orbits for which either system is a proper system in the Sommerfeld sense.

§ 3. *Application to the Resolution of Lines in the Stark Effect.*—Consider an orbit for which at least one of the two conditions (17), (18) is satisfied in the absence of an external field, and therefore for which

$$n_\xi = n_\eta = m/2. \tag{23}$$

If now an electric field is slowly introduced, then since the quantum integrals are adiabatic invariants, (23) will still hold for the corresponding path in the presence of the field. We should, therefore, expect to find components in the spectral resolutions corresponding to such half-integral numbers. It must, however, be remembered that the number and intensity of such components cannot be expected to be large, since the probability of the occurrence of a circular or equatorial path is in general small, and, further, that the occurrence of such a path with a fractional $m/2$ is half this small probability. It is also to be noted that this probability decreases as $n_\xi + n_\eta + n_\psi$ [$= n_r + n_\theta + n_\psi$] increases. Thus a circular or equatorial path ($n_r = 0$; $n_\theta = 0$) is less likely to occur for $n_r + n_\theta + n_\psi = 5$ (say) than for $n_r + n_\theta + n_\psi = 2$. Consequently, ***half-integral components are to be expected much less in the case of the higher than of the lower members of the Balmer series.*** And, finally, the least improbable half-integral paths for hydrogen are the two paths corresponding to

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* Regarding nought as an even integer.

† Orbits calculated on non-relativistic dynamics, for which the condition (18) is satisfied for $r = r_0$ alone, have no corresponding physical reality, and are therefore excluded from $_{\nu,\mathrm{P}}{}^{i}$.

$$n_\xi = n_\eta = 1/2, \qquad n_\psi = 1, \tag{24}$$

which are, in fact, identical in the absence of a field with the circular and equatorial orbits corresponding in spherical polar co-ordinates to

$$n_r = 0, \qquad n_\theta = 1, \qquad n_\psi = 1,$$

and

$$n_r = 1, \qquad n_\theta = 0, \qquad n_\psi = 1$$

respectively.

Table I gives the full scheme of components for H_β calculated on the hypothesis (23), the resolution $\Delta\nu$ being given by

$$\left.\begin{aligned} \Delta\nu &= 3h\mathrm{FN}/8\pi^2 m_0\mathrm{E} \\ \text{and} \quad \mathrm{N} &= (n_2 - n_1)(n_1 + n_2 + n_3) - (m_2 - m_1)(m_1 + m_2 + m_3), \end{aligned}\right\} \tag{25}$$

where F is the field intensity, and n_1, n_2, n_3 are written for n_ξ, n_η, n_ψ respectively.

TABLE I.

$n_1+n_2+n_3 = 2$. Hβ. $m_1+m_2+m_3 = 4$.

Parallel components : $m_3-n_3 = 0$.		Normal components : $m_3-n_3 = \pm 1$.	
m_1 m_2 m_3 → n_1 n_2 n_3.	N.	m_1 m_2 m_3 → n_1 n_2 n_3.	N.
2 0 2 → 0 0 2	8	1 0 3 → 0 0 2	4
1 1 2 → 0 0 2	0	2 0 2 → 0 1 1	10
3 0 1 → 0 1 1	14	2 0 2 → 1 0 1	6
3 0 1 → 1 0 1	10	1 1 2 → 0 1 1	2
2 1 1 → 1 0 1	6	2 1 1 → 0 0 2	4
2 1 1 → 0 1 1	2	3 0 1 → 0 0 2	12
3 0 1 → ½ ½ 1	12	2 0 2 → ½ ½ 1	8
2 1 1 → ½ ½ 1	4	1 1 2 → ½ ½ 1	0
1½ 1½ 1 → 0 1 1	2	½ ½ 3 → 0 0 2	0
1½ 1½ 1 → ½ ½ 1	0	1½ 1½ 1 → 0 0 2	0

In the tables transitions leading to negative values of W are omitted for brevity. These values are obtained by interchanging n_1, n_2 and m_1, m_2 simultaneously in every case. The components above the dotted line in Table I correspond to integral values of the quantum numbers only. Those below the line involve half-integers. The top part of the table is identical with Sommerfeld's* results. In the lower part the components of orders 4, 12, and 0, 8 are added to the p– and n– groups respectively. Now *it is these additional components which represent the exact deficiency of Sommerfeld's tables* when compared with Stark's results.* Table I is in excellent agreement with experiment. The only deviation occurs in the case of the p– components of order 14, which have not been observed. These arise from whole-number transitions.

Further, if the restriction $n_1 = n_2$ for half-integers is removed, it can easily be verified that no additional components arise: the new transitions ensuing merely give rise to components which already exist in Table I for each of the two respective types of polarization. It is, however, improbable that such free use of half-integers for n_1 and n_2 is permissible—first owing to the lack of any theoretical justification for it, and, secondly, because it would lead to a number of components in the case of the other members of the Balmer series, which are not likely to have all escaped observation.

It is seen, on the other hand, from Table I that the bracketed transitions in which fractional numbers occur only in the single set $(n_1, n_2, n_3) = (\frac{1}{2}, \frac{1}{2}, 1)$

TABLE II.

$(n_1, n_2, n_3) = (\frac{1}{2}, \frac{1}{2}, 1)$.

	H_α.		H_γ.		H_δ.	
	m_1 m_2 m_3.	N.	m_1 m_2 m_3.	N.	m_1 m_2 m_3.	N.
Parallel components	1 1 1	0	2 2 1	0	5 0 1	30
	2 0 1	6	3 1 1	10	4 1 1	18
			4 0 1	20	3 2 1	6
Normal components	1 0 2	3	2 1 2	5	4 0 2	24
			3 0 2	15	3 1 2	12
					2 2 2	0

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* *Loc. cit.*, p. 291, Tables 29 and 30.

completely account for the additional components, which complete Sommerfeld's tables for H_β, referred to above. *This is in full accordance with the above theory*, since the two orbits defined by this set of numbers are more likely to occur than any other half-integral orbits. Table II gives the additional components for H_α, H_γ, H_δ respectively arising from transitions in which fractional numbers occur only in this single set, these being the most probable half-integral components to appear for the respective Balmer " lines." Needless to say, experimental investigation with a view to the detection of these fresh components would be highly desirable.

§ 4. The accumulation of evidence quoted in § 1, together with the results of the other two sections, suggests a general form*

$$J_i = \int_0 \pi_i \, dq_i = (m_i/\mu_i)h, \qquad i = 12, \ldots \tag{26}$$

for the quantum conditions, where m_i and μ_i are integers. Here

$$\pi_i = p_i + eA_i, \qquad i = 1, 2, \ldots \tag{26A}$$

the q's and p's being Hamiltonian co-ordinates, e the charge on the particle in question, and A the corresponding four-vector potential; the sign $\int_0$ denotes integration over the complete period of libration of the independent variable. *This hypothesis possesses the special merit of leading to the classical law of least action as a limiting case.* Thus from (26) we have

$$\Delta J_i = \Delta \int_0 \pi_i \, dq_i = \Delta \, (m_i/\mu_i) \, h, \tag{27}$$

and the classical laws corresponding to (26) and (27) respectively are

$$J_i = \int_0 \pi_i \, dq_i = C_i \tag{26'}$$

$$\delta J_i = \delta \int_0 \pi_i \, dq_i = 0 \tag{27'}$$

where C_1, C_2, ... are arbitrary constants. Now let m_i and μ_i each increase indefinitely, so that

$$\underset{\left(\substack{m_i \to \infty \\ \mu_i \to \infty}\right)}{\mathrm{Lt}} \; [m_i/\mu_i] \, h = C_i \tag{28}$$

then

$$\underset{\left(\substack{m_i \to \infty \\ \mu_i \to \infty}\right)}{\mathrm{Lt}} \; [\Delta \, (m_i/\mu_i)] = \mathrm{Lt} \left[\frac{\mu_i \Delta m_i - m_i \Delta \mu_i}{\mu_i \, (\mu_i + \Delta \mu_i)}\right]$$
$$= 0,$$

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* See W. Wilson, *loc. cit.*

provided that Δm_i and $\Delta \mu_i$ are both finite ; thus

$$\underset{\left(\substack{m_i \longrightarrow \infty \\ \mu_i \longrightarrow \infty}\right)}{\mathrm{L}t} [\Delta \mathrm{J}_i] = 0, \tag{29}$$

and it is seen that the classical laws (26′) and (27′) now hold as limiting cases of the quantum laws (26) and (27) respectively. The question of the actual behaviour of the quantum integers m_i, μ_i in a specified problem and the way it is linked up with the classical laws of radiation still, however, remains open to investigation. In the case of the simple hydrogen atom in the absence of external fields there is little doubt that m_i/μ_i assumes integral values alone. The considerations put forward in this paper point out to half integers within the domain of the phenomena considered. Could it be that the general form (26) holds the key to the behaviour of more complicated atoms and molecules ?

The Quantum Theory and the Dielectric Constant.

By J. H. Jones, B.Sc., Ph.D., Assistant Lecturer in Physics, King's College.

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Introduction.

The change of energy of an atom of hydrogen when submitted to an electric field has been calculated by Epstein.* If W denotes the total energy of an atom, then the change in energy Δ W, due to the field F, is given by

$$\Delta \mathrm{W} = -\frac{3h^2\mathrm{F}}{8\pi^2 m\mathrm{E}}(n_2 - n_1)(n_1 + n_2 + n_3) + \frac{17e^2\mathrm{F}^2}{(16\pi\mathrm{R_H})^2\, m}\mathrm{Z}(n_1, n_2, n_3),$$

where $\mathrm{R_H}$ is Rydberg's constant for hydrogen and

$$\mathrm{Z}(n_1, n_2, n_3) = (n_1+n_2+n_3)^6 \left\{1 - \frac{3}{17}\left(\frac{n_1 - n_2}{n_1+n_2+n_3}\right)^2 - \frac{9}{17}\left(\frac{n_3}{n_1+n_2+n_3}\right)^2\right\},$$

and n_1 and n_2 are parabolic quantum numbers and n_3 is the equatorial quantum number.

The first term in the expression for Δ W represents the potential energy of the natural doublet of the orbit, and, of course, disappears for a circular orbit ($n_1 = n_2 = 0$). It corresponds to the quantity $\tfrac{3}{2}a\epsilon\mathrm{F}\cos\theta$ in the case of a Kepler orbit, for $\tfrac{3}{2}a\epsilon$ is the distance of the mean-time position of the electron from the nucleus and θ is the angle between the major axis of the ellipse and the direction of the field, whilst "a" and "ε" represent the semi-major axis and the eccentricity respectively. For circular orbits (or more generally $n_1 = n_2$) the first term will disappear, and we are left with the small term of the second degree in F. This quantity, when integrated over unit volume of the gas, becomes identical with $\frac{K-1}{8\pi}F^2$, where K is the dielectric constant of the medium. As far as the writer is aware, nobody has as yet given this meaning to this term in the Stark effect as worked out by Epstein.

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* 'Ann. der Physik,' vol. 51, p. 184 (1916).

Application to Atomic Hydrogen.

For atomic hydrogen in the normal state we have $n_1 + n_2 + n_3 = 1$, and as n_3 cannot be less than unity, $n_1 = n_2 = 0$, and consequently

$$\frac{K-1}{8\pi}F^2 = \frac{N\,17e^2F^2}{(16\pi R_H)^2 m} Z(n_1, n_2, n_3) \tag{1}$$

where N is the number of atoms per unit volume. This gives (K − 1) for atomic hydrogen

$$= \frac{4\pi N h^6}{64\pi^6 Z^4 e^6 m^3},$$

where $Z = E/e = 1$, and writing $\frac{h^2}{4\pi^2 m e^2} = a_1$ (the radius of the first Bohr circle for hydrogen) we get

$$K - 1 = 4\pi N (a_1)^3.$$

The same result can be obtained for the case $n_1 + n_2 + n_3 = 1$ by making use of the consequences of spatial quantising. Assuming, following Sommerfeld,* that the plane of the orbit will be perpendicular to the direction of the electric field, and disregarding the alternate possible position, when the orbital plane is parallel to the field direction, then the effect of the field will be to displace the orbital plane, as shown in fig. 1.

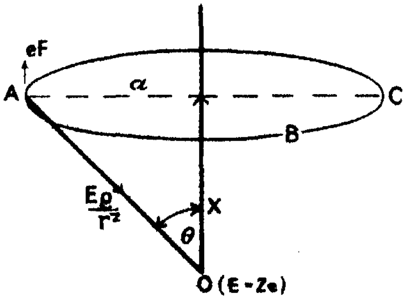

FIG. 1.

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* 'Atomic Structure and Spectral Lines,' English Edition, p. 283.

ABC is the orbital plane and O the nucleus, which is now at a distance x from the plane of the orbit, which is still a circular orbit.

For equilibrium we get $eF = \frac{Ee}{r^2}\cos\theta = \frac{Eex}{r^3}$.
Also

$$\frac{Ee\sin\theta}{r^2} = mw^2a, \quad i.e., \frac{Eea}{r^3} = mw^2a,$$

giving

$$r^3 = \frac{Ee}{mw^2} \quad \text{and} \quad x = \frac{Fr^3}{E} = \frac{eF}{mw^2}.$$

The polarization $P = \Sigma ex = Nex$, if N = number of atoms per unit volume. Therefore

$$P = \left(\frac{K-1}{4\pi}\right)F = \frac{Ne^2F}{mw^2}, \quad \text{giving } K-1 = \frac{4\pi Ne^2}{mw^2}.$$

Putting in the value $w = \frac{8\pi^3e^4Z^2m}{h^3}$ we get the same result as above.

We see from the value of (K — 1) that the atom of hydrogen behaves in a uniform electric field like a perfectly conducting sphere of radius equal to that of the first Bohr circle. An assumption of this kind was made by Mossotti, and he deduced approximate values (lower limits) of the diameter of molecules which are in fair agreement with values obtained from the kinetic theory.*

Putting in the values of N ($2{\cdot}705 \times 10^{19}$) and a_1 — ($0{\cdot}532 \times 10^{-8}$) we get (K — 1) for atomic hydrogen $= 5{\cdot}12 \times 10^{-6}$.

When the total quantum number $(n_1 + n_2 + n_3)$ is greater than unity, then in general the expression for the potential energy of an electron contains a term in the first degree in F. We have to assume, however, that when averaged over the atom (or over a large number of atoms) this term disappears, in other words that $\Sigma(n_2 - n_1)$ is zero. This seems to be the case for all atoms in the normal state, for no substance is known which has a resultant electric moment, that is, there is no effect corresponding to paramagnetism.†

This leaves us the term in the second degree, and we have

$$\frac{K-1}{8\pi} = \Sigma\frac{17e^2n^6}{(16\pi R)^2m}\left[1 - \frac{3}{17}\left(\frac{n_1-n_2}{n_1+n_2+n_3}\right)^2 - \frac{9}{17}\left(\frac{n_3}{n_1+n_2+n_3}\right)^2\right]. \quad (2)$$

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* *Cf.* Jeans, 'Dynamical Theory of Gases,' p. 332, 3rd Edition.

† Prof. O. W. Richardson has pointed out to me that the result $\Sigma(n_2 - n_1) = 0$ is required by the fact that the complete symmetry of the Stark effect extends not only to the frequencies but also to the intensities of the components.

The summation sign means that we must take account of all the electrons in the atom and also for all the atoms in unit volume. When the azimuthal quantum number is greater than unity, then the equatorial number n_3 has a choice of values. For example, if $n_a = 2$ ($n_a =$ azimuthal quantum number) then n_3 can be either 1 or 2, but not zero.*

Combined with these possibilities for n_3 we have choice of values for n_1 and n_2 and if we make the assumption that these are equally probable we can evaluate the right-hand side of (2). This is also the necessary condition that the term in the first degree in F should vanish, for $\Sigma\,(n_1 - n_2)$ is zero.

In general then, when the azimuthal quantum number is n_a we have n_a possible positions for the axis of resultant moment of momentum, given by

$$\cos\theta = \frac{1}{n_a},\ \frac{2}{n_a},\ \ldots\ \frac{n_a}{n_a},$$

where θ is the angle between the axis mentioned above and the direction of the electric field.

Case of a Circular Orbit with very large Quantum Number.

The equatorial number n_3 can have all values $1, 2, 3 \ldots n$; where n is the total quantum number of the orbit in question. Further, these values are assumed to be equally probable.

Let us suppose that n is an even number, so that when $n_3 = 1$, $(n_1 - n_2)$ can assume the following values $\pm 1, \pm 2, \pm 3 \ldots \pm (n-1)$. Similarly when $n_3 = 2$, $(n_1 - n_2)$ can have the values $0, \pm 1, \pm 2, \pm 3 \ldots \pm (n-2)$. When $n_3 = 3$, then $(n_1 - n_2) = \pm 1, \pm 2, \ldots \pm (n-3)$, and similarly for other values of $n_3 = 4, 5, \ldots n$, we require the mean value of

$$\left[1 - \frac{3}{17}\left(\frac{n_1 - n_2}{n_1 + n_2 + n_3}\right)^2 - \frac{9}{17}\left(\frac{n_3}{n_1 + n_2 + n_3}\right)^2\right].$$

When $n_3 = 1$, its value is

$$\left[1 - \frac{3}{17}\left\{\left(\frac{1}{n}\right)^2 + \left(\frac{2}{n}\right)^2 + \cdots + \left(\frac{n+1}{n}\right)^2\right\}\frac{2}{2\,(n-1)} - \frac{9}{17}\left(\frac{1}{n}\right)^2\right].$$

When $n_3 = 2$ it is

$$\left[1 - \frac{3}{17}\left\{\left(\frac{0}{n}\right)^2 + \left(\frac{1}{n}\right)^2 + \ldots \left(\frac{n-2}{n}\right)^2\right\}\frac{2}{2n-3} - \frac{9}{17}\left(\frac{2}{n}\right)^2\right],$$

---

* *Cf.* Sommerfeld, p. 283, *op. cit.*

with corresponding values for $n = 3, 4, \ldots, n$. The mean value is

$$\begin{aligned}
&\frac{1}{n}\left\{\left[1 - \frac{3}{17}\,\frac{2}{2\,(n-1)}\,\frac{(n-1)\,(n)\,(2n-1)}{6n^2} - \frac{9}{17}\left(\frac{1}{n}\right)^2\right]\right.\\
&\qquad + \left[1 - \frac{3}{17}\,\frac{2}{2n+3}\,\frac{(n-2)\,(n-1)\,(2n-3)}{6n^2} - \frac{9}{17}\left(\frac{2}{n}\right)^2\right]\\
&\qquad + \left[1 - \frac{3}{17}\cdot\frac{2}{2n-5}\,\frac{(n-3)\,(n-2)\,(2n-5)}{6n^2} - \frac{9}{17}\left(\frac{3}{n}\right)^2\right]\\
&\qquad + \ldots +\\
&\qquad \left.+ \left[1 - \frac{3}{17}(0) - \frac{9}{17}\left(\frac{n}{n}\right)^2\right]\right\}\\
&= \frac{1}{n}\left[n - \frac{3}{17}\left\{\frac{n\,(2n-1)}{6n^2} + \frac{4}{6n^2}\left(\overline{n-2}^2 + \overline{n-4}^2 + \ldots + \overline{n-n}^2\right)\right\}\right.\\
&\qquad\qquad\qquad \left. - \frac{9}{17}\left\{\left(\frac{1}{n}\right)^2 + \left(\frac{2}{n}\right)^2 + \ldots \left(\frac{n}{n}\right)^2\right\}\right]\\
&= \frac{1}{n}\left[n - \frac{3}{17}\left\{\frac{n\,(2n-1)}{6n^2} + \frac{8}{3}\,\frac{1}{n^2}\left(1^2 + 2^2 + \ldots \left(\frac{n-2}{2}\right)^2\right)\right\}\right.\\
&\qquad\qquad\qquad \left. - \frac{9}{17}\,\frac{1}{n^2}\left\{1^2 + 2^2 + \ldots + n^2\right\}\right]\\
&= \left[1 - \frac{3}{17}\left\{\frac{2n-1}{6n^2} + \frac{8}{3}\,\frac{1}{n^3}\,\frac{\left(\frac{n-2}{2}\right)\left(\frac{n}{2}\right)(n-1)}{6}\right\}\right.\\
&\qquad\qquad\qquad \left. - \frac{9}{17}\left\{\frac{1}{n^3}\,\frac{n\,(n+1)\,(2n+1)}{6}\right\}\right].
\end{aligned}$$

As n approaches infinity, this reduces to $\dfrac{13\frac{2}{3}}{17}$.

When "n" is very large the number of directions possible for the axis of resultant moment of momentum becomes very large, and in the limit all directions are equally probable. This is what we would expect on the classical theory, and we should get

$$\left(\frac{\mathrm{K}-1}{8\pi}\right) = \frac{17e^2\mathrm{N}n^6}{(16\pi\mathrm{R})^2 m}\,\frac{13\frac{2}{3}}{17},$$

i.e. $\mathrm{K} - 1 = 1{\cdot}707 \quad 4\pi\mathrm{N}\,(a_1)^3$.

Case when "n" is odd.—Averaging for all possible cases we get the same result as above. The method of averaging is exactly similar to that given when "n" is even.

The Dielectric Constant of Atomic Hydrogen on the Classical Theory.

The quantum theory requires that the plane of the orbit be perpendicular to the direction of the field. On the classical theory all directions are equally probable for the normal to the orbital plane and, of course, we would expect a different value for (K − 1). We have already deduced this as a limiting case of the quantum theory by supposing that the total quantum number is very large. We also assumed that the orbit was circular when no applied field was present. A different method can be used in this particular case, viz. all directions equally probable, as demanded by the classical theory. The method used is exactly the same as that employed by Gans* for molecular hydrogen. For this purpose cylindrical co-ordinates are used, and we write

$$r_1 = a(1+\eta_1); \qquad \phi_1 = wt + \phi_0 + \eta_2; \qquad z = a\eta_3,$$

"a" being the radius of the undisturbed circular orbit ($F = 0$) and "w" the periodicity; then $ds^2 = r_1^2\,d\phi_1^2 + dr_1^2 + dz_1^2$, and

$$\left(\frac{ds}{dt}\right)^2 = r_1^2\left(\frac{d\phi_1}{dt}\right)^2 + \left(\frac{dr_1}{dt}\right)^2 + \left(\frac{dz_1}{dt}\right)^2.$$

The kinetic energy of the moving electron is

$$\mathrm{T} = \frac{ma^2}{2}\{w^2 + 2\eta_1 w^2 + \eta_1^2 w^2 + 2\dot{\eta}_2 w + 4\eta_1\dot{\eta}_2 w + 2\eta_1^2\dot{\eta}_2 w + \eta_1^2$$
$$+ \dot{\eta}_2^2 + \dot{\eta}_3^2 + 2\eta_1\dot{\eta}_2^2 + \eta_1^2\dot{\eta}_2^2\},$$

and the potential energy

$$\mathrm{U} = \frac{\mathrm{E}e}{(r_1^2+z_1^2)^{\frac{1}{2}}} = \frac{\mathrm{E}e}{a^2\{(1+\eta_1)^2 + a^2\eta_3^2\}^{\frac{1}{2}}} = \frac{\mathrm{E}e}{a}\{\overline{1+\eta_1}^2 + \eta_3^2\}$$
$$= \frac{\mathrm{E}e}{a}\left\{1 - \eta_1 - \frac{\eta_1^2}{2} - \frac{\eta_3^2}{2}\right\}.$$

We consider small displacements about the equilibrium position and using Lagrange's equations

$$\frac{\partial}{\partial t}\left(\frac{\partial \mathrm{T}}{\partial \dot{r}}\right) - \frac{\partial \mathrm{T}}{\partial r} + \frac{\partial \mathrm{U}}{\partial r} = \text{External Force}$$

and two other equations for ϕ and z.

$$\frac{\partial \mathrm{T}}{\partial \dot{r}_1} = \frac{1}{a}\frac{\partial \mathrm{T}}{\partial \dot{\eta}_1}; \qquad \frac{\partial \mathrm{T}}{\partial r_1} = \frac{1}{a}\frac{\partial \mathrm{T}}{\partial \eta_1}; \qquad \frac{\partial \mathrm{U}}{\partial r_1} = \frac{1}{a}\frac{\partial \mathrm{U}}{\partial \eta_1}; \qquad \frac{\partial}{\partial t}\left(\frac{\partial \mathrm{T}}{\partial \dot{r}_1}\right) = \frac{1}{a}\frac{\partial}{\partial t}\left(\frac{\partial \mathrm{T}}{\partial \dot{\eta}_1}\right).$$

Consequently, we get for the "r" equation of motion

$$ma^2\ddot{\eta}_1 - 2ma^2\dot{\eta}_2 w = -ea\mathrm{E}_x\cos(wt + \phi_0).$$

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* 'Zeit. für Physik,' vol. 9, p. 81 (1922).

E_x is the component of the electric force in the x direction (assumed to be in the plane of the orbit), so that $E_x \cos(wt + \phi_0)$ is the component of the electric force in the r direction at any instant "t."

In a similar manner we get the "ϕ" equation of motion

$$\phi_1 = wt + \phi_0 + \eta_2,$$
$$d\phi_1 = wdt + d\eta_2,$$
$$d\dot{\phi}_1 = w + \dot{\eta}_2.$$

The equation of motion is

$$\frac{\partial}{\partial t}\left(\frac{\partial T}{\partial \dot{\eta}_2}\right) - \frac{\partial T}{\partial \eta_2} + \frac{\partial U}{\partial \eta_2} = eaE_x \sin(wt + \phi_0),$$

giving

$$ma^2\ddot{\eta}_2 + 2ma^2w\dot{\eta}_1 = eaE_x \sin(wt + \phi_0).$$

Similarly, for the z equation of motion we get

$$ma^2\ddot{\eta}_3 + \frac{Ee}{a}\eta_3 = -eaE_z.$$

The first two equations are

$$\ddot{\eta}_1 - 2w\dot{\eta}_2 = -\frac{eE_x}{ma}\cos(wt + \phi_0)$$

$$\ddot{\eta}_2 + 2w\dot{\eta}_1 = \frac{eE_x}{ma}\sin(wt + \phi_0).$$

If we suppose the applied field to be varying with the time, we can investigate the dispersion of atomic hydrogen. Setting $E_x = K\cos st$, $E_z = L\cos st$, we have

$$\ddot{\eta}_1 - 2w\dot{\eta}_2 = -\frac{eK}{ma}\{\cos(\overline{w+s}\,t + \phi_0) + \cos(\overline{w-s}\,t + \phi_0)\}$$

$$\ddot{\eta}_2 + 2w\dot{\eta}_1 = \frac{eK}{ma}\{\sin(\overline{w+s}\,t + \phi_0) + \sin(\overline{w-s}\,t + \phi_0)\}.$$

The most general solution is

$$\eta_1 = \frac{Ke}{maw^2}[A_1\cos\{\overline{w+s}\,t + \phi_0\} + A_2\cos\{\overline{w-s}\,t + \phi_0\}]$$

$$\eta_2 = \frac{Ke}{maw^2}[B_1\sin\{\overline{w+s}\,t + \phi_0\} + B_2\sin\{\overline{w-s}\,t + \phi_0\}].$$

Substituting in the differential equations and putting

$$x = s/w,$$

we get by equating the coefficients of the cosine and sine terms to zero the following equations for the constants A_1; A_2; B_1; B_2;

$$\begin{aligned} A_1(1+x)^2 + 2B_1(1+x) &= 1; \\ A_2(1-x)^2 - 2B_2(1-x) &= 1; \\ B_1(1+x)^2 + 2A_1(1+x) &= -1; \\ B_2(1-x)^2 + 2A_2(1-x) &= -1. \end{aligned}$$

When $s = 0$ (steady field) $x = 0$, then the values of the constants are $A_1 = -1$, $A_2 = -1$, $B_1 = 1$, $B_2 = 1$. The "z" equation of motion is

$$ma^2\ddot{\eta}_3 + \frac{Ee}{a}\eta_3 = -eaE_2 = -eaL\cos st.$$

Remembering that $Ee/a = ma^2w^2$, we have

$$\ddot{\eta}_3 + w^2\eta_3 = -\frac{eL}{ma}\cos st.$$

The solution is

$$\eta_3 = C\cos st, \qquad \text{where} \qquad C = \frac{e}{maw^2}\frac{L}{(1-x^2)}.$$

The components of polarization are

$$\begin{aligned} P_x &= -er_1\cos\phi_1 \\ &= -ea\,\{\eta_1\cos(wt+\phi_0) - \eta_2\sin(wt+\phi_0)\} \\ P_y &= -er\sin\phi_1 \\ &= -ea\,\{\eta_1\sin(wt+\phi_0) - \eta_2\sin(wt+\phi_0)\} \\ P_z &= -ez_1 = -ea\eta_3. \end{aligned}$$

Substituting the values found above for η_1, η_2, η_3; we get*

$$\begin{aligned} P_x &= \frac{Ke^2}{2mw^2}[(B_1-A_1)+(B_2-A_2)]\cos st \\ P_y &= -\frac{Ke^2}{2mw^2}[(B_1-A_1)-(B_2-A_2)]\sin st \\ P_z &= \frac{Le^2}{mw^2}\frac{1}{1-x^2}\cos st. \end{aligned}$$

If we make the direction of the transverse field quite arbitrary, *i.e.* free ourselves of the assumption that it is in the direction of the x axis, we can write

$$\begin{aligned} P_x &= \frac{e}{mw^2}\left(g'E_x - \frac{f}{s}\frac{\partial E_y}{\partial t}\right) \\ P_y &= \frac{e}{mw^2}\left(g'E_y + \frac{f}{s}\frac{\partial E_x}{\partial t}\right) \\ P_z &= \frac{e}{mw^2}gE_z, \end{aligned}$$

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* *Cf.* Gans, p. 84, *loc. cit.*

and

$$g' = \tfrac{1}{2}[(B_1 - A_1) + (B_2 - A_2)]$$

$$f = \tfrac{1}{2}[(B_1 - A_1) - (B_2 - A_2)]$$

$$g = \frac{1}{1 - x^2}.$$

The refractive index " n " is given by the formula

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N}{3} \frac{e}{mw^2} \frac{g + 2g'}{3},$$

and the dielectric constant K is obtained from this expression, when $x = 0$, giving

$$K - 1 = 4\pi N \frac{e}{mw^2} \cdot \frac{5}{3} \qquad [g = 1, \quad g' = 2].$$

Putting in the value of w^2 given by the quantum theory, we get

$$K - 1 = \frac{5}{3} \frac{4\pi N n^6 h^6}{64\pi^6 e^2 E^4 m^3} = \frac{5}{3} \frac{4\pi N (a_n)^3}{Z^4}.$$

In this last expression (a_n) denotes the radius of the Bohr circle of the n^{th} order and $Z = E/e$. For atomic hydrogen $n = 1$, $Z = 1$, so that

$$K - 1 = \tfrac{5}{3} 4\pi N (a_1)^3 = 1 \cdot 667 \;.\; 4\pi N (a_1)^3.$$

The method of the quantum theory, by passing into the limit when n is large, gives $1 \cdot 707 \times 4\pi N \, (a_1)^3$. The two should, of course, agree, though the difference is only a small percentage error, and considering that the two methods are entirely different, and that both solutions are approximations, it is satisfactory that they are so near. It is important to notice that the quantum theory makes the value of $(K - 1)$ for atomic hydrogen to be $4\pi N \, (a_1)^3$, whilst the classical theory requires it to be $5/3 \; 4\pi N \, (a_1)^3$. Now that atomic hydrogen can be produced in quantities it might be possible to decide between these two expressions.

Application to other Gases.

Although the expression for Δ W given above is only rigidly true for the hydrogen atom and ionised helium, it is perhaps allowable to apply it to more complex atoms on the assumption that the field of force is of the form $\frac{(Z - S) e}{r^2}$ where Ze is the nuclear charge and " S " is the screening constant. On account of the rapid decrease of $(Z - S)$ with the order of the shell, we need only consider the electrons in the outermost shell in calculating $K - 1$, because of the factor $(Z-S)^4$ in the denominator. In addition, we have the factor $(n_1+n_2+n_3)^6$ in the numerator, and this will also tend to make the outermost shell the predominant one.

Instead of calculating $K-1$ we have assumed the experimental values for this quantity and deduced the screening constant for the different energy levels. The calculation is given in full for xenon, assuming Bohr's structure for the atom. Bohr assigns four 5_1 and four 5_2 orbits to the outer shell, which has a total quantum number 5. The suffixes denote the azimuthal quantum number. As mentioned above, we must find the mean value of

$$\left[1-\frac{3}{17}\left(\frac{n_1-n_2}{n_1+n_2+n_3}\right)^2-\frac{9}{17}\left(\frac{n_3}{n_1+n_2+n_3}\right)^2\right]$$

for each type of orbit. When $n_a=1$ (azimuthal number) then $n_3=1$ and n_1-n_2 can have the following values :—0, ± 1, ± 2, ± 3, ± 4.

There are four orbits for which $n_a=1$, and consequently $n_3=1$, and their contribution to the value of the factor given above will be

$$4\left[1-\frac{3}{17}\left\{\left(\frac{0}{5}\right)^2+\left(\frac{1}{5}\right)^2+\left(\frac{2}{5}\right)^2+\left(\frac{3}{5}\right)^2+\left(\frac{4}{5}\right)^2\right\}\frac{2}{9}-\frac{9}{17}\left(\frac{1}{5}\right)^2\right]=\frac{1584}{17\times 25}.$$

When $n_a=2$, n_3 can be either 1 or 2, and both are equally probable. The contribution of these orbits will be

$$\frac{4}{2}\left\{2-\frac{3}{17}\left\{\left(\frac{0}{5}\right)^2+\left(\frac{1}{5}\right)^2+\ldots\left(\frac{4}{5}\right)^2\right\}\frac{2}{9}+\left\{\left(\frac{1}{5}\right)^2+\left(\frac{2}{5}\right)^2+\left(\frac{3}{5}\right)^2\right\}\frac{2}{6}\right.$$
$$\left.-\frac{9}{17}\left[\left(\frac{1}{5}\right)^2+\left(\frac{2}{5}\right)^2\right]\right\}=\frac{1542}{17\times 25},$$

so that

$$\frac{K-1}{8\pi}=\frac{e^2N5^6}{(16\pi R)^2 m}\left[\frac{3026}{25}\right].$$

Putting in the values of N and R and m, and solving for $Z-S$, we get

$$Z-S=9\cdot 68,\text{ and as } Z=54,\ S=44\cdot 32.$$

Proceeding in this way for the other gases and vapours, we get the figures tabulated below.

The screening numbers are approximately constant for the different levels and only gradually decrease with the number of electrons in the outer shell. For the M shell, for instance, the screening constant diminishes from 12·43 for argon to 11·54 for phosphorus. The ratio of the effective nuclear charge to the total quantum number of the shell in question is approximately constant for those elements whose outer shell is complete, and this ratio gradually decreases as the number of electrons diminishes.

Screening Constants for the Outer Shell of Different Elements.

Element.	Atomic Number.	$(K-1)10^4$	Level of Outer Shell.	Eff. Nuclear Charge.	"S."	$\frac{Z-S}{n}$	"S" by Sommerfeld's Formula.
Xenon	54	13·78	O	9·68	44·32	1·93	48·80
Iodine	53	38·40*	,,	8·69	44·31	1·76	48·30
Krypton	36	8·50	N	7·77	28·13	1·94	30·80
Bromine	35	22·50*	,,	7·06	27·94	1·76	30·30
Argon	18	5·68	M	5·57	12·43	1·89	12·80
Chlorine	17	15·36	,,	4·99	12·01	1·66	12·30
Sulphur	16	20·92	,,	4·52	11·53	1·51	11·83
Phosphorus	15	46·48	,,	3·46	11·54	1·15	11·38
Neon	10	1·34	L	4·17	5·83	2·08	4·80
Oxygen	8	5·43	,,	3·23	4·77	1·61	3·83
Nitrogen	7	5·94	,,	2·99	4·01	1·50	3·38

* Calculated from the refractive index for the D line of Na.

The last column gives the screening constants calculated by the formula introduced by Sommerfeld.[*] The screening number "S" has been obtained from the relation $S = p + Sq$, where p is the number of inner electrons and Sq is the screening effect of the remaining electrons in the outer shell, calculated on the assumption that the electrons are symmetrically distributed on the circumference of a circle. This, however, is only a very rough approximation.

It is important to remember that the treatment given by Epstein is only rigidly true when very strong fields are used and the perturbations of the orbits due to the applied field are large compared with those due to relativity effects. It is only in this case that it is possible to use classical mechanics and to quantise with parabolic co-ordinates. The dielectric constants we have used have mostly been obtained from dispersion experiments when the applied fields are small, while strictly the dielectric constants we deal with are those corresponding to very strong fields. However, we have no reason to suppose that the dielectric constants alter considerably with the strength of the applied field.

Further, a small change in the value of $(K - 1)$ would not have much effect on the value of the screening constant, as the effective nuclear charge $(Z - S)$ is proportional to $\frac{1}{(K-1)^{\frac{1}{4}}}$. In any case, the relativity effects will get less pronounced as the order of the outer shell increases. In fig. 2 the screening numbers are graphed against the atomic numbers. It is seen that the points corresponding to the inert gases lie approximately on a straight line, whilst the other values are displaced slightly to one side of the line. These screening numbers are in reasonable agreement with those obtained with the approximate formula of Sommerfeld.

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[*] *Loc. cit.*, p. 76.

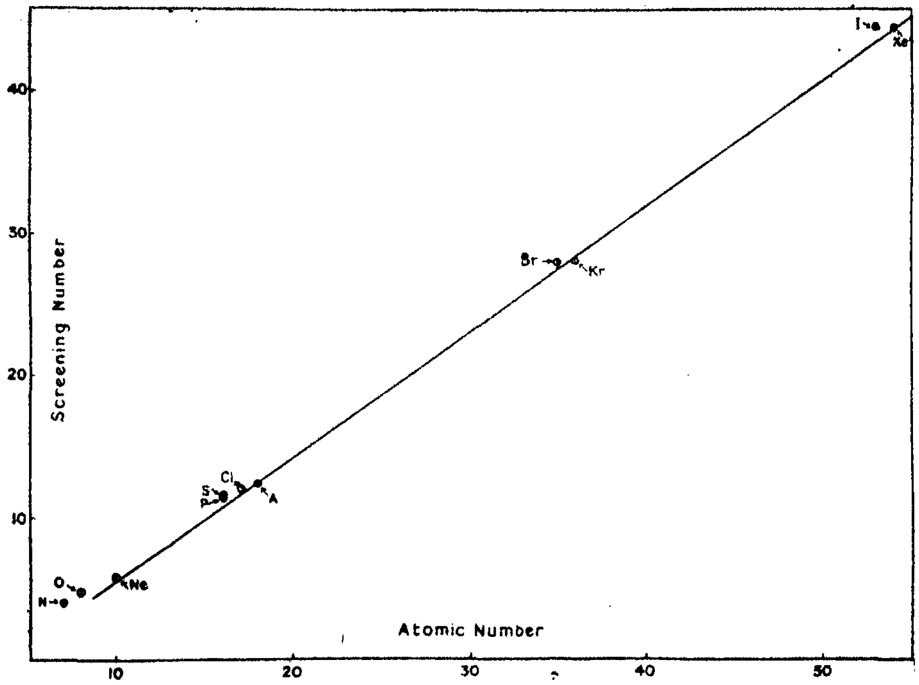


Fig. 2.

In conclusion, the writer wishes to express his gratitude to Prof. O. W. Richardson for his helpful criticism.

The Analysis of the Absorption Spectrum of Naphthalene Vapour.—Structure and Activation of the Molecule of Naphthalene.

By VICTOR HENRI, D.Sc., Professor of Physical Chemistry, University, Zurich, and HENRY DE LÀSZLÒ, B.A.

(Communicated by Prof. Sir E. Rutherford, F.R.S.—Received March 29, 1924.)

[PLATE 6.]

I.—INTRODUCTORY.

Classification of the Absorption Spectra of Vapours.

The study of the absorption spectrum of a substance in the state of vapour enables us to widen our knowledge of the movements and structure of molecules. The ultra-violet absorption spectra of a large number of different substances in the state of vapour show a great variety of structures. We must find a general classification which holds good for all types observed till now, and this classification must be based on the mechanism causing absorption spectra. Bohr's theory shows us the general mechanism of all absorption and emission phenomena.

An atom or molecule in the normal state possesses a value of internal energy E^0. Under the influence of different agents, such as radiation, thermal motion, electrical discharges or chemical reactions, etc., this energy can be changed. This change in internal energy is called the " activation " or excitation of the atom or molecule. When the activation is produced by absorption of radiation (frequency $= \nu$), the second postulate of Bohr then says that $h\nu = E' - E^0$.

In the case of molecules, we must consider three kinds of motion: (1) The gravitation of the electrons in their various orbits. (2) The vibration of the atoms or groups of atoms. (3) The rotation of the molecule itself. We must now examine each kind of motion separately.

1. *Electrons.*—All the results of the spectra of the elements as well as the X-ray spectra of compounds, lead us to believe that electronic motion is quantified. The motion of all electrons in the normal molecule possesses a certain energy E_e^0. When the molecule is excited the electrons pass to new stationary orbits, the energy thus becoming $E_e' > E_e^0$. The " *electronic activation energy* " is equal to $E_e' - E_e^0$. There will be just as many values for this energy as there are stationary orbits in the particular molecule in question.

2. *Atoms.*—The vibratory motion of the atoms or groups of atoms possesses a

certain normal atomic energy E_a^0. On activation of the molecule the vibration can change. We can distinguish two types of change :—

(*a*) The vibratory motion is quantified. In this case, the energy of the atomic vibrations changes suddenly in the form of jumps taking up a whole series of stationary values E_a', E_a'', E_a''' . . . The "*atomic activation energy*" will therefore have a whole series of distinct values $E_a' - E_a^0$, $E_a'' - E_a^0$, $E_a''' - E_a^0$ .... According to Planck's theory, the vibratory motion is quantified if the atoms or groups of atoms vibrating in a molecule are oppositely charged. ("Intramolecular ionisation" of J. J. Thomson.)

(*b*) The vibratory motion is *not* quantified. Hence the energy of atomic vibration can vary continuously and can take any value either smaller or greater than E_a^0, the frequency of this distribution being determined by an exponential law of the type of Maxwell's. The energy of atomic activation can thus vary continuously within smaller or larger limits, these limits being determined by the labile state of the molecule.

3. *Molecule.*—The rotation of the molecule in the normal state has an energy of $E_m^0 = \frac{1}{2}J_0\omega_0^2$, where J_0 is the moment of inertia and ω_0 the angular velocity. In this case also we shall have to differentiate two types of motion :—

(*a*) The rotatory motion is quantified and obeys Bohr's correspondence principle. One would therefore get a series of distinct values : $E'_m = \frac{1}{2}J_1\omega_1^2$, $E_m'' = \frac{1}{2}J_2\omega_2^2 \ldots$, with the quantification conditions

$$J_0\omega_0 = \frac{m_0 h}{2\pi}, \quad J_1\omega_1 = \frac{m_1 h}{2\pi} \ldots, \quad \text{hence } E_m^0 = \frac{m_0^2 h}{8\pi^2 J_0},$$

$$E_m' = \frac{m_1^2 h}{8\pi^2 J_1}, \quad E_m'' = \frac{m_2^2 h}{8\pi^2 J_2} \ldots,$$

where m_0, m_1, $m_2 \ldots$ are whole numbers.

By the correspondence principle, a molecule may pass either from the state of rotation m to $(m - \mathrm{I})$, or from $(m - \mathrm{I})$ to m or lastly from m to m. In the last case the moment of inertia only changes by reason of a change in the electronic or atomic configuration in the molecule.

Hence the "*activation energy of rotation*" will have three series of branches having different values :—

$$\text{Positive branch : } \frac{(m - \mathrm{I})^2 h^2}{8\pi^2 J_1} - \frac{m^2 h^2}{8\pi^2 J_0} \ldots \mathrm{R};$$

$$\text{Negative branch : } \frac{m^2 h^2}{8\pi^2 J_1} - \frac{(m - \mathrm{I})^2 h^2}{8\pi^2 J_0} \ldots \mathrm{P};$$

$$\text{Zero branch : } \frac{m^2 h^2}{8\pi^2 J_1} - \frac{m^2 h^2}{8\pi^2 J_0} \ldots \mathrm{Q}.$$

(*b*) In the second type the rotatory movements of the molecule are not quantified, but vary continuously. The energy of rotation may take any value distributed about a central value according to an exponential law.

The mechanism of absorption obeys the second postulate of Bohr, as a result of which the frequency absorbed

$$1/\lambda = \frac{E_e' - E_e^0}{h \,.\, c} + \frac{E_a' - E_a^0}{h \,.\, c} + \frac{E_m' - E_m^0}{h \,.\, c}$$

where c, the speed of light, $= 3 \,.\, 10^{10}$ cm./sec.

Taking into consideration the various possibilities of activation of the molecule, we can identify three types of absorption spectra.

Type A.—*Spectra with fine structure. Triple quantification.*—In this case all forms of motion are quantified; the molecule shows a triple periodicity corresponding to combinations amongst themselves of :—

(*a*) Electronic activation energy $E'_e - E_e^0$, $E_e'' - E_e^0$, $E_e''' - E_e^0$ ... ;

(*b*) Atomic activation energy $E_a' - E_a^0$, $E_a'' - E_a^0$, $E_a''' - E_a^0$ ... ;

(*c*) Molecular activation energy $E_m' - E_m^0$, $E_m'' - E_m^0$, $E_m''' - E_m^0$ ... .

(*a*) is of the order 10,000 . hc; (*b*) of the order of a few hundred times hc; (*c*) of a few unit times hc.

The absorption spectrum will therefore consist of a certain number of *groups* (corresponding to electronic activation), each group being made up of a series of bands (atomic activation), each band showing a fine structure which consists of a certain number of very fine and closely spaced bands or lines (activation due to molecular rotation).

The different values of E_e are distributed according to a complicated law which till now has not been formulated. We can put

$$\frac{E_e' - E_e^0}{h \,.\, c} = A, \quad \frac{E_e'' - E_e}{h \,.\, c} = B, \quad \frac{E_e''' - E_e^0}{h \,.\, c} = C, \; \ldots .$$

The value for the energy of vibration of atoms or atomic groups is :—

$$E = n \,.\, hc\,(\alpha + \alpha' \,.\, n + \ldots) + p \,.\, hc\,(\beta + \beta' \,.\, p + \ldots) + q \,.\, hc\,(\gamma + \gamma' \,.\, q + \ldots) + \ldots,$$

where α, β, γ, ..., are the vibration frequencies ; α'; β', γ', ..., are second-order terms which show that the vibrations are not harmonic, and n, p, q, ... are whole numbers.

On passing from the normal state E^0 to the excited state E', we get

$$\begin{aligned}\frac{1}{\lambda} = \frac{E' - E^0}{h.c.} = \left.\begin{matrix}A\\B\\C\\\vdots\end{matrix}\right\} &+ n'(\alpha + \alpha' n' + \ldots) - n^0(\alpha + \alpha' n^0 + \ldots) \\ &+ p'(\beta + \beta' p' + \ldots) - p^0(\beta + \beta' p^0 + \ldots) \\ &+ q'(\gamma + \gamma' q' + \ldots) - q^0(\gamma + \gamma' q^0 + \ldots) + R(m) \\ &+ P(m) + Q(m),\end{aligned}$$

or

$$\frac{1}{\lambda} = \left.\begin{matrix}A\\B\\C\\\vdots\end{matrix}\right\} + n\,.\,\alpha + \ldots + p\,.\,\beta + \ldots + q\,.\,\gamma + \ldots + R(m) + P(m) + Q(m),$$

n, p, q being either positive or negative whole numbers.

The variation of the molecular rotation is represented by three series of values which determine the distribution of the lines in each band :—

$$R(m) = \frac{h}{8\pi^2 c}\left\{\frac{I}{J_1} - \frac{2m}{J_1} + m^2\left(\frac{I}{J_1} - \frac{I}{J_0}\right)\right\}, \qquad m = 1, 2, 3, \text{ etc.}$$

$$P(m) = \frac{h}{8\pi^2 c}\left\{-\frac{I}{J_0} + \frac{2m}{J_0} + m^2\left(\frac{I}{J_1} - \frac{I}{J_0}\right)\right\}, \qquad m = 1, 2, 3, \text{ etc.}$$

$$Q(m) = \frac{m^2 h}{8\pi^2 c}\left(\frac{I}{J_1} - \frac{I}{J_0}\right), \qquad m = 0, 1, 2, 3, \text{ etc.}$$

The absorption spectra of the vapours of following substances examined by one of us show a fine structure: Sulphur, CS_2, SO_2, glyoxal, acrolein, cetene, cyanogen, phosgene, benzene, fluor-, chlor- and brombenzene, toluene, para-xylene, furfurol, etc., etc. We will see that one-half of the spectrum of naphthalene vapour obeys the same law of triple quantification.

Type B.—*Spectra with Narrow Continuous Bands not showing Fine Structure. Double Quantification.*—Absorption spectra belonging to this type are made up of series of narrow bands having a width of 5 to 10 Ångström. These bands are quite continuous, showing that only the electronic and atomic motions are quantified while the molecular rotation is not.

This type of absorption spectrum has been found by one of us for the vapours of ammonia, the amines, thiophene, diacetyl, etc. We shall see that the portion of the spectrum of naphthalene further in the ultra-violet belongs to this type.

Type C.—*Spectra with Broad, Continuous Bands. Simple Quantification.*—Absorption spectra of this class exhibit broad bands from 100 to 300 Å wide and sometimes more. These bands are quite continuous. This indicates that only the electronic motion is quantified, while that of the atoms and molecule varies continuously without quantification.

Absorption spectra of this type are shown by the vapours of the saturated ketones and aldehydes, saturated acids, β, γ, δ, diketones and unsaturated ketones where the carbonyl group is in the β, γ, or δ position to the ethylene group. As examples of simpler molecules, one of us has found with Mr. Teves, very wide continuous bands for H_2S and COS, and with Mr. Howell for $Ni(CO)_4$, $SnCl_4$, CCl_4, etc.

Evolution of the Absorption Spectrum of Vapours.

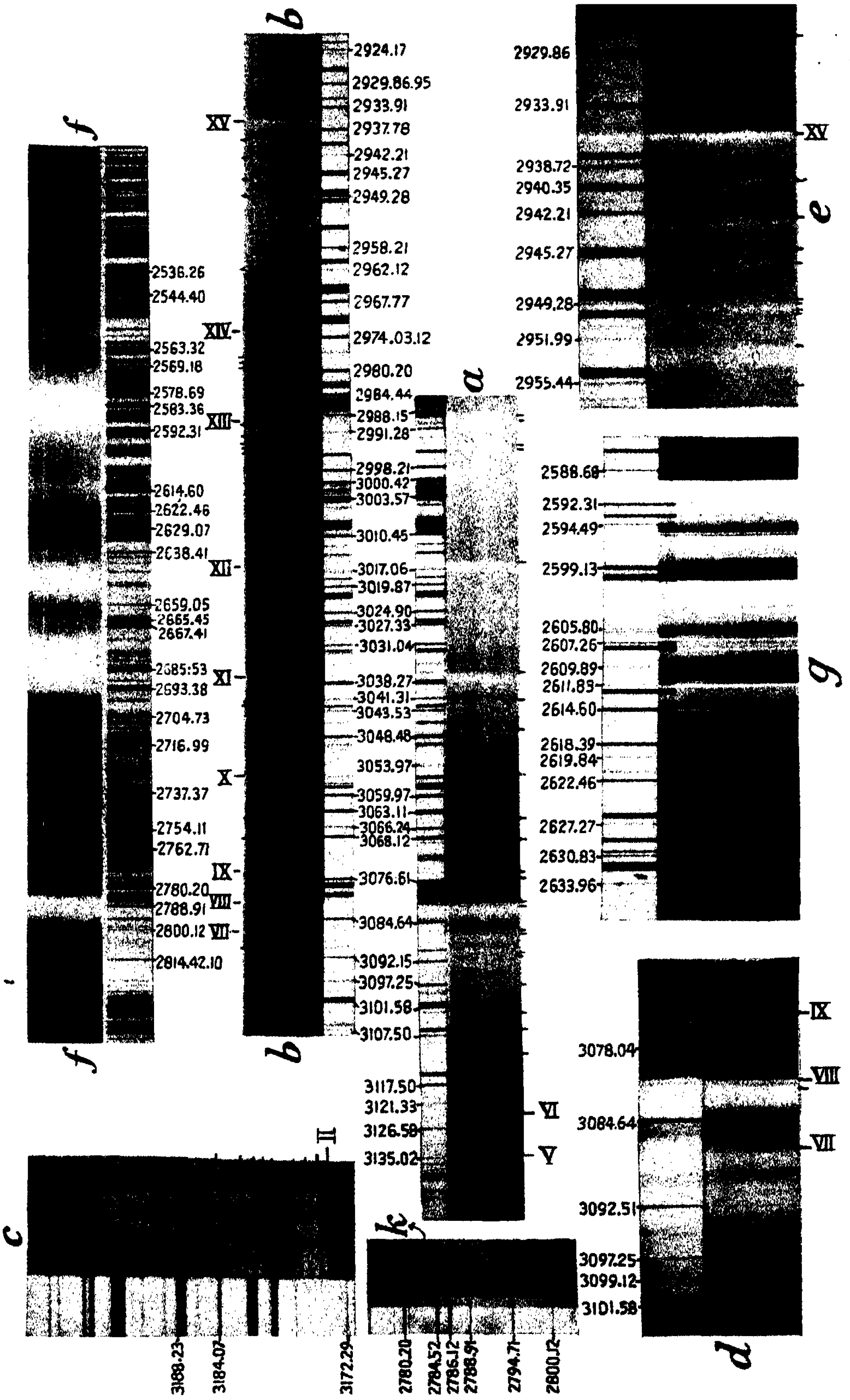
When we examine the absorption spectrum of a vapour from the red to the extreme ultra-violet ($\lambda = 1900$ Å), one of us finds a new phenomenon which seems to be fairly general. The spectrum changes towards the higher frequencies. In a large number of substances we find in the less refrangible part a spectrum of type A with narrow bands resolvable into fine lines. Then, as we approach higher frequencies the fine structure disappears, leaving continuous narrow bands. At higher frequencies still we find only very broad continuous bands.

As a typical case, we can give that of acrolein, which gives a vast number of narrow bands resolvable into very regularly-spaced fine lines between 4000 and 3300 Å. One of us has measured more than 500 fine lines in this interval. Towards $\lambda = 3300$ the fine structure disappears, and between $\lambda = 3300$ and 3000 Å we get a series of narrow continuous bands having a width of 4 to 10 Å. Above $\lambda = 3000$ Å the absorption spectrum of the vapour is absolutely continuous. Below $\lambda = 2450$ Å we find a very strong and broad absorption band, with its maximum at $\lambda = 2000$ Å, and showing no fine structure.

Another very clear example has been found by one of us with Mr. Teves. Sulphur vapour at 260° gives a spectrum containing a fine structure consisting of thousands of fine lines between 4000 and 2800 Å. The interval between the lines is of the order of 1/20 Å, and the lines are distributed in very regular series. Similar spectra are obtained with CS_2 and SO_2.

Below 2800 the spectrum of sulphur vapour changes suddenly. The fine structure disappears completely, and we get a series of narrow bands with a width of 2 to 5 Å, which become hazier and broader as we approach the ultra-violet end.

We find the same phenomenon for naphthalene vapour: between 3200 and 2820 Å the spectrum consists of a number of narrow bands which are resolved


b
2924.17
2929.86.95
2933.91
2937.78
2942.21
2945.27
2949.28
2958.21
2962.12
2967.77
2974.03.12
2980.20
2984.44
2988.15
2991.28
2998.21
3000.42
3003.57
3010.45
3017.06
3019.87
3024.90
3027.33
3031.04
3038.27
3041.31
3043.53
3048.48
3053.97
3059.97
3063.11
3066.24
3068.12
3076.61
3084.64
3092.15
3097.25
3101.58
3107.50
XV
XIV
XIII
XII
XI
X
IX
VIII
VII
f
2536.26
2544.40
2563.32
2569.18
2578.69
2583.36
2592.31
2614.60
2622.46
2629.07
2638.41
2659.05
2665.45
2667.41
2685.53
2693.38
2704.73
2716.99
2737.37
2754.11
2762.71
2780.20
2788.91
2800.12
2814.42.10
e
2929.86
2933.91
2938.72
2940.35
2942.21
2945.27
2949.28
2951.99
2955.44
XV
a
3117.50
3121.33
3126.58
3135.02
VI
V
g
2588.68
2592.31
2594.49
2599.13
2605.80
2607.26
2609.89
2611.83
2614.60
2618.39
2619.84
2622.46
2627.27
2630.83
2633.96
d
3078.04
3084.64
3092.51
3097.25
3099.12
3101.58
IX
VIII
VII
c
II
3188.23
3184.07
3172.29
k
2780.20
2784.52
2786.12
2788.91
2794.71
2800.12

(*To face p.* 667.)

into very fine and closely-spaced bands or lines. Below 2820 Å we get continuous narrow bands. We give in Plate 6 some photographs of the spectrum of naphthalene vapour: *a* and *b* shows the general distribution and appearance of the spectra between 3135 and 2924 Å. The various bands have been numbered V, VI ... XV. An iron spark was used as comparison spectrum. The fine structure of bands II, VII, VIII, IX and XV are shown on the enlargements *c*, *d* and *e*. Figure *f* shows the absorption spectrum in the ultra-violet between 2814 and 2500 Å, where a series of narrow *continuous* bands are to be seen. Fig. *g* shows the band at 2789 Å photographed with the same dispersion as bands II, VII, etc., in the figures *c*, *d* and *e*. As comparison we give in figure *k* a portion of a benzene band between 2588 and 2633 which shows the fine structure very clearly.

This change in the absorption spectrum of a body as we approach the higher frequencies can also be seen in the cases of glyoxal, diacetyl, cetene, crotonic aldehyde, benzene derivatives, pyrrol, furane, etc., etc. Several authors (Wood, Ribaud, etc.) have observed in the case of the absorption spectra of the vapours of Cl, Br, and I that they consist of a number of very fine rays at the less refractory end of the spectrum, and that below a certain limit broad continuous bands make their appearance.

We have to ask ourselves what the theoretical meaning of these sudden changes in the spectrum is. We can now give only a provisional hypothesis for this phenomenon.

A molecule A B consists of atoms or atomic groups A, B, which are bound together. The bond between A and B is produced by certain electrons belonging to A and B which either revolve in common orbits round A and B or have orbits in any symmetrical position. As a result we may get a displacement of the electrons so that A becomes positive and B negative. Thus we get what J. J. Thomson calls "intramolecular ionisation." A quantification of the vibratory movements of A and B is the result and gives rise to series of narrow bands and lines.

When rays of low frequency are absorbed, the electrons pass to other orbits which are not far removed from the normal orbits, thus causing but little change in the intramolecular ionisation. But if rays of high frequency are absorbed, the electronic orbits are greatly affected, the electrons move away from the centres A and B, so that the bond between A and B is greatly loosened and at the same time a re-arrangement of the electrons takes place. The rotatory movement of the molecule, and then the atomic or atomic group vibrations, cease to be quantified.

The knowledge of the limits where these alterations take place in the spectrum enables us to calculate the energy required to bring about these intramolecular changes. For example, in the case of naphthalene we find that as soon as the intramolecular energy rises above 101,000 calories per grm. mol. (since $\frac{2 \cdot 85}{\lambda} = \frac{2 \cdot 85 \,.\, 10^8}{2820} = 101{,}000$) the rotatory motion of the molecule ceases to be quantified, but the vibrations of the atomic groups still remain so. The broad and continuous bands make their appearance much further on. In fact, the ionisation potential of naphthalene vapour corresponds to about 10 volts (Boucher, 'Physical Rev.,' 1922), which represents an increase of internal energy of 230,000 cal. gr./mol., so that the limit of the continuous spectrum would be 1235 Å.

II.—PRACTICAL DETAILS FOR OBTAINING THE ABSORPTION SPECTRUM OF NAPHTHALENE VAPOUR.

Spectrographs.—Two spectrographs were used in this piece of research. (*a*) Hilger's spectrograph E_2 with a quartz Cornu prism 41 mm. high and a face length of 65 mm., and two lenses of 610 mm. focal length. The length of the spectrum between 3200 and 2200 Å is 97 mm. (*b*) Hilger's spectrograph E_1, with a lens of 70 mm. clear aperture and 170 cms. focal length, and a 30° quartz prism, with a face 98 mm. long and 57 mm. high, the second face being coated with a tin-mercury amalgam. It is of the "Littrow" form. This gives a very fine dispersion, the length of the spectrum between 3200 and 2200 Å being 270 mm. Spectra taken with this spectrograph may be measured with an accuracy of 0·01 to 0·02 Å.

Source of Light.—To obtain a continuous ultra-violet spectrum we make use of a high frequency spark under water, using Cu or Al electrodes as already described by one of us.* The primary current is 60 volts and 20 amperes interrupted 600 times a second. (See diagram, fig. 1.) Two sets of condensers C_1 and C_2 2, 3 . 10^{-3} micro-farad are connected in parallel. S_1 is an air-gap spark, length being 15 to 20 mm., and S_2 is the water spark between firmly mounted electrodes of 8 mm. diameter whose distance apart can be accurately regulated by means of a micrometer screw. The tank holds three litres of distilled water and is made of teak. The electrodes are mounted 5 cms. below level of the water, the spark taking place at a distance of 10 to 15 mm. from the quartz window *q*. All connections are made of Cu wire, and are led as straight as possible in order to reduce the self-induction to a minimum. The frequency of the oscillatory discharge has been directly measured and is found to be in the neighbourhood of a million times a second. This spark gives a very bright light and is fairly uniform. An exposure of 3 to 5 minutes is sufficient to give a continuous spectrum reaching from the visible to 2100 Å. As comparison spark we use a condensed iron spark with a self-inductance 1, 2 . 10^{-5} Henry in the secondary circuit in order to obtain very fine lines and to remove the air lines.

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* 'Physikal. Zeitschr.,' 1913.

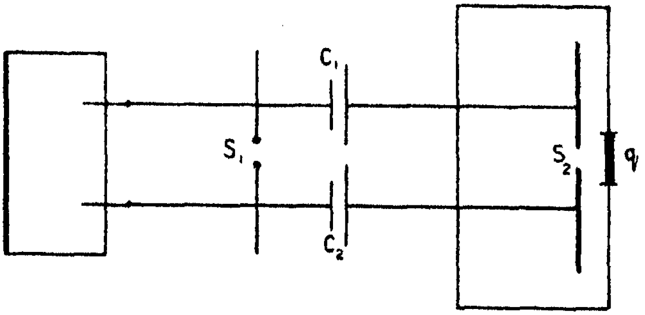

FIG. 1.

Measurement of the Spectra.—The spectra were measured on two comparators, one by Jobin and the other built in Göttingen on the Hartmann system. The iron lines were identified by means of the secondary and tertiary standards of the International Astronomical Union, Rome, 1922, and (till 3370 Å) by the values given in Exner and Haschek's tables. The latter were converted to International Ångström Units and all were reduced to vacuum with the aid of Fowler's tables ('Report on Series in Line Spectra,' London, 1922, p. 81). All wave-lengths are therefore given in International Ångström units reduced to vacuum.

Absorption Tube.—For the purpose of studying the absorption of vapours at various temperatures, we have made a tube entirely of fused quartz (see fig. 2). The substance is placed in the small hollow B of the inner tube. This tube is closed at the ends by four transparent quartz windows, which have been well polished. The two end chambers were completely evacuated. The length of the column of vapour was 30 cm. The central tube is surrounded by another concentric tube of quartz, the two being melted together to form a sort of condenser, the annular space being filled with a liquid, preferably of low specific heat and high boiling point, such as tetralin, which may be safely used till 250° C. Nickel-chrome wire is wound round the outer tube, the whole being thus electrically heated. A vacuum of less than 1/10,000 mm. is produced in the apparatus with the aid of two mercury-vapour Langmuir pumps. A large number of absorption spectra of naphthalene vapour were taken at temperatures ranging from 20° C. to 150° C.

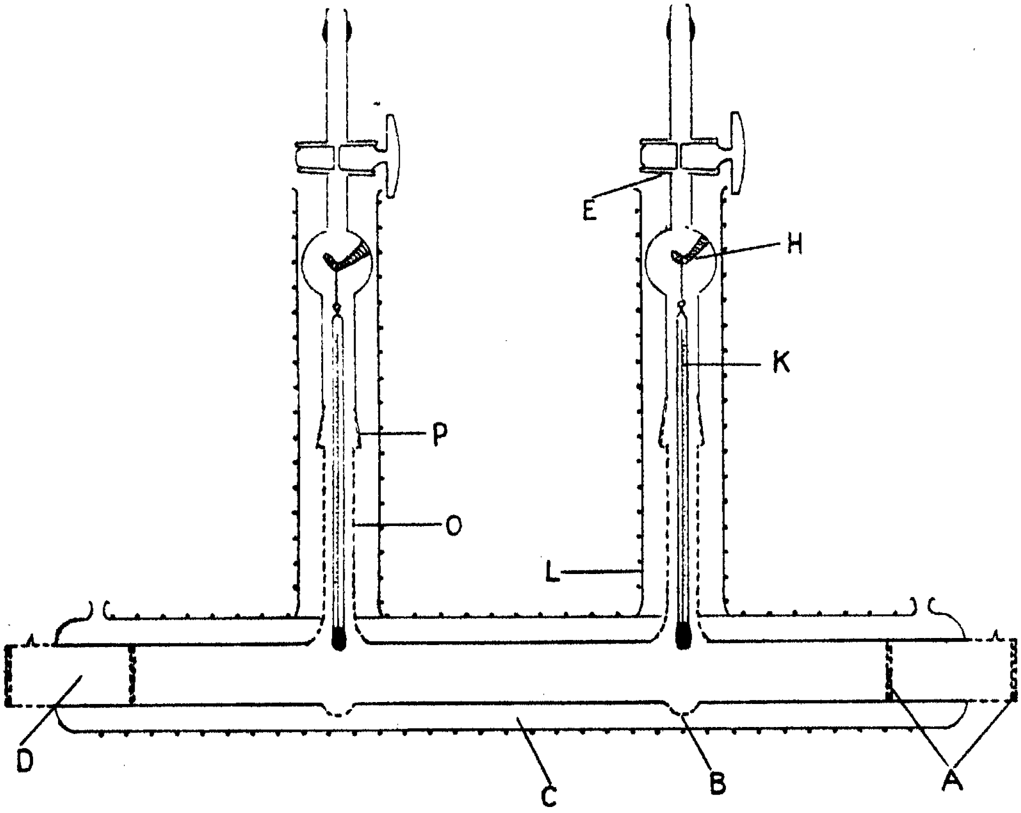

Fig. 2.

Intensity Determination of the Absorption Bands.—For many theoretical calculations it is of importance to know the intensity of the absorption bands in absolute units. One of us has worked out a method for the case of vapours. This consists of photographing the vapour spectrum at various pressures and noting the minimum pressure at which the band in question appears. The intensity of the band will be given by the inverse of the pressure at which it appears. In order to obtain results in absolute units, so as to be able to compare them with the molecular absorption of the substance in solution, we express the intensity of the band as the inverse of the molecular concentration reduced to a layer 1 cm. wide, at which the band appears. The concentration of the vapour when reduced to a layer 1 cm. thick is equal to $c = \frac{p \, . \, d}{17{,}030}$ since 22,400 atmospheres = 17,030 mm., and the intensity of the absorption band is equal to $i = \frac{17{,}030}{p \, . \, d}$, where p is measured in mm. and d in cm. When put in this form, we can compare the intensity of a vapour band with the molecular absorption coefficient in solution ϵ, which is given by the relation $J = J_0 \cdot 10^{-\epsilon . c . d}$. In the case of our absorption tube $d = 30$ cm., the intensity of the bands being equal to $i = \frac{5680}{p}$. The vapour pressure of naphthalene may be deduced from the temperature, according to Crafts[*] and Thomas.[†]

The following table gives the vapour pressure of naphthalene vapour with the corresponding band intensities :—

t.	p.	$i = \frac{5680}{p}$.	t.	p.	$i = \frac{5680}{p}$.
°	mm.		°	mm.	
20	0·054	105,000	80	8	710
30	0·13	43,700	90	13	437
35	0·22	25,800	100	20	284
40	0·35	15,620	110	28	206
45	0·53	10,720	120	43	132
50	0·82	6,930	130	64	89
55	1·23	4,630	140	87	65
60	1·84	3,170	150	121	47
70	3·90	1,456	160	165	34

The intensities of the bands therefore vary between 105,000 and 34 units.

III.—DESCRIPTION OF THE ABSORPTION SPECTRUM OF NAPHTHALENE VAPOUR.

When we examine photographs of the absorption spectrum of naphthalene vapour taken through a column 30 cm. thick, at temperature varying from 20° C. to 150° C., we find that at 20° C. four very feeble and ill-defined bands make their appearance, the vapour pressure being $p = 0 \cdot 054$ mm. These bands are situated round 2784, 2750, 2680 and 2644 Å. At $t = 23°$ and $p = 0 \cdot 071$ mm. the same bands increase in intensity and width, at the same time ill-defined bands appear at = 2778, 2740, 2710, 2636, 2613, 2590 and 2560 Å.

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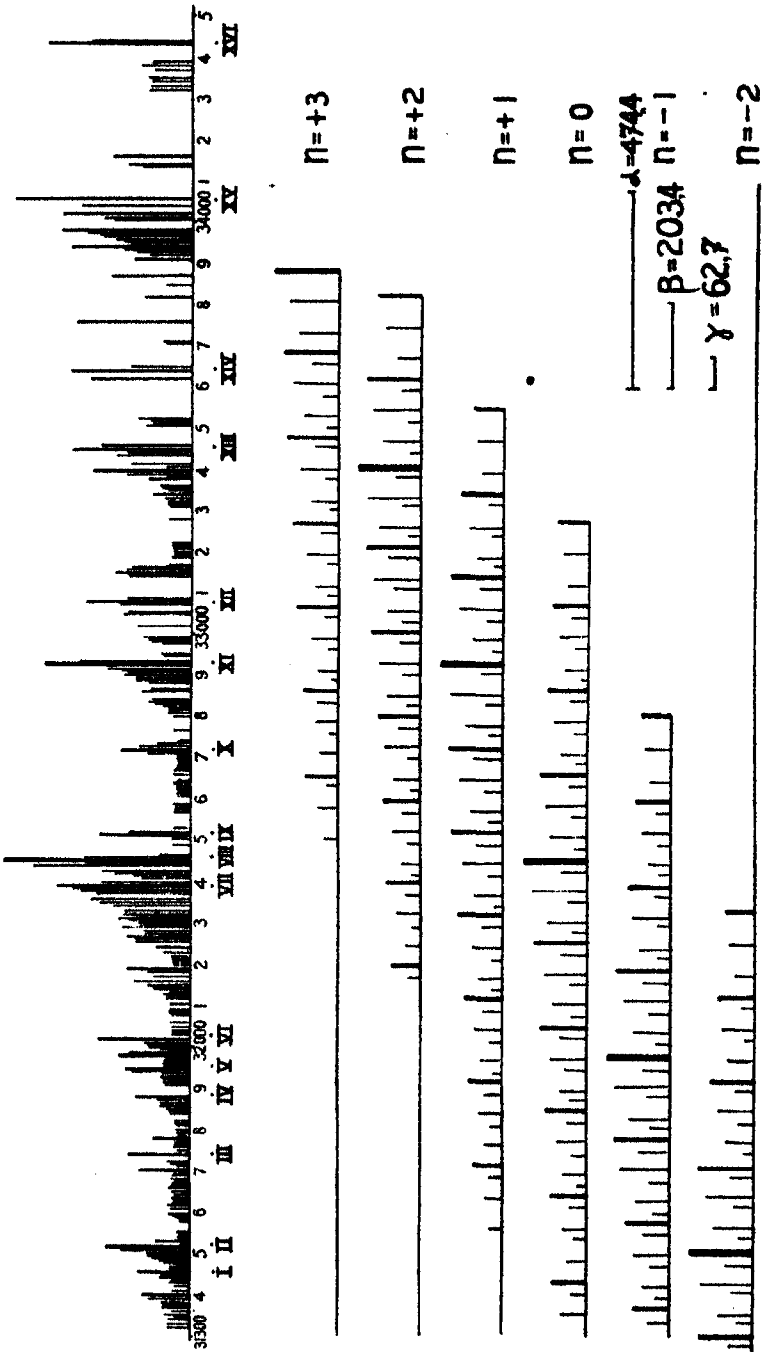
[*] J. M. Crafts, 'Jour. Chim. Phys.,' vol. 11, p. 459 (1913).

[†] J. S. G. Thomas, 'Jour. Soc. Chem. Ind.,' vol. 31, p. 506 (1916).


31500
4
5
6
7
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33000
1
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4
5
6
7
8
9
34000
1
2
3
4
5
I
II
III
IV
V
VI
VII
VIII
IX
X
XI
XII
XIII
XIV
XV
XVI
n=+3
n=+2
n=+1
n=0
n=−1
n=−2
α=4744
β=2034
γ=62,7

Fig. 3.

These bands become intenser and widen as the temperature rises. No new bands could be found till $t = 37°$ C. Photograph *c* was taken at 30° C. In this we see clearly that the bands are quite continuous and exhibit no fine structure. The whole group of these bands we will call A. Their absolute intensity varies from 100,000 to 23,000. Fig. 3 gives a general idea of these bands, indicating their position and intensities. The position of the maxima are shown by vertical lines. Below we give the maxima of the absorption spectrum of naphthalene in hexane solution, which has been measured by one of us with Mr. Steiner.* We see that the solution spectrum is shifted considerably towards the red end with respect to the vapour spectrum.

From 35° C. onwards very narrow bands make their appearance in regions of higher wave-length (Plate 6). These bands belong to group B and number about 400, lying between $\lambda = 2818{\cdot}37$, $1/\lambda = 35481{\cdot}5$, and $\lambda = 3192{\cdot}60$, $1/\lambda = 31322{\cdot}4$ cm.$^{-1}$. The whole spectrum is shown on photograph *b* taken at 68° $p = 3{\cdot}7$ mm., and *a* at 82° $p = 9$ mm.; *c* taken at 105°, $p = 24$ mm., shows the fine structure of bands II and I.

The most intense bands that appear at 35° are the following :—

λ.	I/λ.	Band No.	λ.	I/λ.	Band No.
2823·73	35414·2	XVIII.	3016·09	33155·5	XII.
2840·03	35099·7	XVII.	3036·84	32929·8	XI.
2936·28	34056·7	XV.	3081·15	32455·4	VIII.
2990·27	33441·8	XIII.	3086·84	32395·6	VII.

These bands are the heads of the series of very fine bands, which are obtained at still higher temperatures. They lie on the side of longer wave-length with respect to the band heads, so that each band gives the appearance of being shaded off in fine striations towards the red end of the spectrum.

Between 45° and 60° and $p = 0{\cdot}53$ to $1{\cdot}84$ mm. the following new band heads appear :—

λ.	I/λ.	Band No.	λ.	I/λ.	Band No.
2910·71	34355·9	XVI.	3122·86	32021·9	VI.
2972·76	33638·8	XIV.	3129·42	31954·8	V.
3055·66	32726·2	X.	3137·02	31877·4	IV.
3074·77	32522·8	IX.	3146·63	31780·0	III.

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* V. Henri et P. Steiner, "Absorption des rayons ultra-violets par le naphtalène," 'C. R. Ac. de Sc., Paris,' vol. 175, p. 421, 1922.

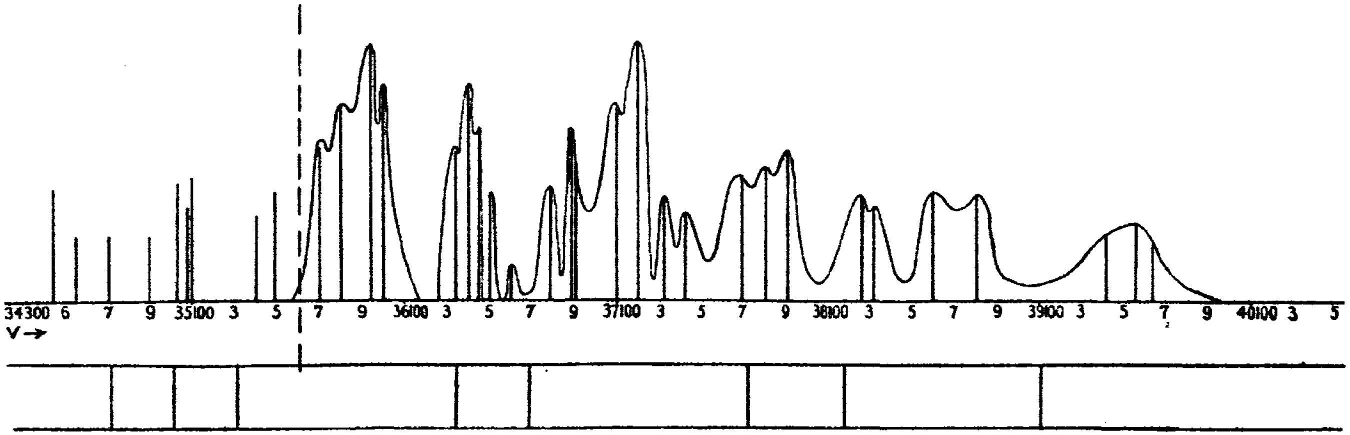

Fig. 4.

At a temperature of 105° $p = 24$ mm. the two last bands II and I appear:—

$$\text{II}\,\lambda = 3173{\cdot}78,\ \text{I}/\lambda = 31508{\cdot}2\,;\quad \text{I}\,\lambda = 3179{\cdot}09,\ \text{I}/\lambda = 31455{\cdot}5.$$

The entire spectrum consists of 18 to 20 bands. Each band can be analysed into twenty or so very fine bands at intervals of about 0·4 Å.

Fig. 4 above gives a general idea of the spectrum between $\lambda = 3192{\cdot}60$ and $\lambda = 2813{\cdot}37$ A. It is impossible to show more than the intense bands owing to the small scale of the drawing. The group of bands B in the vapour spectrum of naphthalene correspond to 12 of the bands that occur in hexane solution. The coefficient of absorption of the solution bands in group B are about 10 times less than those of group A.

IV.—ANALYSIS OF THE ABSORPTION SPECTRUM OF NAPHTHALENE VAPOUR.

The general appearance of the vapour spectrum of naphthalene in group B shows at once that this portion belongs to the first type of spectra with triple quantification. We must, therefore, try to fit it into a formula of the type

$$\frac{\mathrm{I}}{\lambda} = \left.\begin{matrix}\mathrm{A}\\ \mathrm{B}\\ \mathrm{C}\\ \vdots\end{matrix}\right\} + n\,.\,\alpha + p\,.\,\beta + q\,.\,\gamma + \mathrm{R}\,(m) + \mathrm{P}\,(m) + \mathrm{Q}\,(m).$$

The close examination of the spectrum shows that bands VIII, XI, XIII, V, II, all have exactly the same structure; they, therefore, belong to the same series. Certain intervals keep on appearing in the spectrum, thus:—

$$\mathrm{XI} - \mathrm{X} = 32929{\cdot}8 - 32726{\cdot}2 = 203{\cdot}6 \text{ cm.}^{-1}$$

$$\mathrm{X} - \mathrm{IX} = 3276{\cdot}2 - 32532{\cdot}8 = 203{\cdot}4 \text{ cm.}^{-1}.$$

This interval of 203·4 occurs between a large number of other bands. Also the interval between the strong bands VIII and XI, which is equal to 474·4 cm.$^{-1}$ re-occurs between a whole series of other bands. Lastly, a third fundamental interval is found to be 62·7 cm.$^{-1}$.

We can, therefore, represent a large number of the bands including nearly all the more intense ones by the formula:—

$$\mathrm{I}/\lambda = 32455{\cdot}4 + n\,.\,474{\cdot}4 + p\,.\,203{\cdot}4 + q\,.\,62{\cdot}6.$$

Band 32455·5 is chosen as our zero as it is the most intense. $n = -2, -1, 0, +1, +2$, and $+3$. $p =$ whole numbers between -4 and $+4$ and q between -6 and $+2$.

The following tables show some of the observed and calculated values for the naphthalene vapour bands. They agree well to a first approximation, and it is certain that the agreement would be still better if terms of the type n^2, p^2, q^2 were to be introduced. (Tables A and B, over-leaf.)

We represented the distribution of the bands in series in fig. 3; the band heads are thickly drawn.

This formula does not account for quite all the bands; No. XV is the most important exception. It can be subdivided into five equidistant series with $\Delta 1/\lambda = 40$ cm.$^{-1}$. This is clearly shown in photographs *b* and *e*. Other exceptions are bands XVI, XVII, XVIII in the ultra-violet end. For these bands another formula with other periods could be found.

Table A.

p.	$n = -2$.		$n = -1$.		$n = 0$.		$n = +1$.		$n = +2$.	
	Calculated.	Obs.	Calculated.	Obs.	Calculated.	Obs.	Calculated.	Obs.	Calculated.	Obs.
− 4	30693·0	—	31167·4	—	31641·8	45·2	32116·2	—	32590·6	89·3
− 3	30896·4	—	31370·8	70·7	31845·2	45·4	32319·6	18·4	32794·0	—
− 2	31099·8	—	31574·2	—	32048·6	—	32523·0	22·8	32997·4	—
− 1	31303·2	—	31777·6	80·0	32252·0	54·4	32726·4	26·2	33200·8	01·0
0	31506·6	08·2	31981·0	79·5	*32455·4*	*55·4*	32929·8	29·8	33404·2	03·7
+ 1	31710·0	07·8	32104·4	05·4	32658·8	59·8	33133·2	35·1	33607·6	—
+ 2	31913·4	13·2	32307·8	07·1	32862·2	58·6	33336·6	39·9	33811·0	—
+ 3	32116·8	20·9	32511·2	09·5	33065·6	—	33540·0	—	34014·4	13·4
+ 4	32320·2	18·4	32714·6	15·2	33269·0	—	33743·4	—	34217·8	—

Table B.

q.	$n = 0$.	$p = 0$.	$n = +1$	$p = 0$.	$n = 0$.	$p = +1$.
	Calculated	Observed.	Calculated.	Observed.	Calculated.	Observed.
− 6	32079·2	79·6	32543·6	40·8	32292·6	—
− 5	32141·9	41·2	32606·3	05·8	32355·3	55·3
− 4	32204·6	02·6	32669·0	68·3	32408·0	09·9
− 3	32267·3	65·1	32731·7	31·5	32470·7	—
− 2	32330·0	30·0	32804·4	04·6	32533·4	33·1
− 1	32392·7	92·9	32867·1	70·2	32596·1	95·7
0	*32455·4*	55·4	*32929·8*	29·8	*32658·8*	59·8
+ 1	32518·1	18·4	32992·5	—	32721·5	23·0
+ 2	32580·8	82·4	33055·2	55·3	32784·2	—
	$n = -1$.	$p = +1$.	$n = -2$.	$p = +2$.	$n = 0$.	$p = +2$.
− 6	31728·2	29·5	31537·2	37·6	31469·0	70·2
− 5	31790·9	—	31599·9	99·7	31531·7	34·1
− 4	31853·6	54·6	31662·6	60·4	31594·4	97·1
− 3	31916·3	—	31725·3	23·1	31657·1	54·1
− 2	31979·0	79·5	31788·0	86·2	31719·8	19·8
− 1	32041·7	40·6	31850·7	49·5	31782·5	81·5
0	*32104·4*	05·4	*31913·4*	13·2	*31845·2*	45·4
+ 1	32167·1	67·3	31976·1	—	31907·9	—
+ 2	32229·8	—	32038·8	37·1	31970·6	—

The above-mentioned formula contains three periods : $\alpha = 474 \cdot 4$, $\beta = 203 \cdot 4$, $\gamma = 62 \cdot 7$ cm.$^{-1}$. These periods represent the vibration frequency of the various groups of atoms in the naphthalene molecule. It is impossible to allot any one period to one group of atoms. In order to do this we have begun to study the absorption spectra of a number of naphthalene derivatives in order to see how the periods vary with the substituting groups.

One of us* has found two periods for benzene vapour where $a = 921 \cdot 4$ and $\beta = 159$ cm.$^{-1}$. Benzene derivatives (toluene, fluor-, chlor- and brom-benzenes and para-xylene) have vapour spectra which can be well expressed by three periods. Thus for toluene $a = 932 \cdot 5$, $\beta = 263$, $\gamma = 180$, and for chlorbenzene $a = 963 \cdot 7$, $\beta = 443$, $\gamma = 60$.

It is of interest to note in this connection that the main period 474·4 of naphthalene is about half that of benzene and its mono-derivatives. One of us has suggested that this frequency interval is due to the vibration of the two halves of the benzene molecule (C_3H_3), the one with respect to the other. This is in accordance with J. J. Thomson's observation ('Rays of Positive Electricity') that negatively charged C_3H_3 groups were found on introducing benzene vapour into his discharge tube. Perhaps in the case of naphthalene the frequency $a = 474 \cdot 4$ is caused by the coupled vibration of the two benzene nuclei.

Fine Structure.—The preceding formula accounts for the distribution of the main bands, and we shall now see whether the fine structure can be represented by the formulæ

$$\mathrm{P}\,(m) = \frac{h}{8\pi^2 c}\left[\frac{1}{\mathrm{J}_1} - \frac{2m}{\mathrm{J}_1} + m^2\left(\frac{1}{\mathrm{J}_1} - \frac{1}{\mathrm{J}_0}\right)\right] = c_1 - 2mc_1 + m^2 c_2,$$

$$\mathrm{R}\,(m) = \frac{h}{8\pi^2 c}\left[-\frac{1}{\mathrm{J}_0} + \frac{2m}{\mathrm{J}_0} + m^2\left(\frac{1}{\mathrm{J}_1} - \frac{1}{\mathrm{J}_0}\right)\right] = -c_0 + 2mc_0 + m^2 c_2,$$

$$\mathrm{Q}\,(m) = \frac{m^2 h}{8\pi^2 c}\left(\frac{1}{\mathrm{J}_1} - \frac{1}{\mathrm{J}_0}\right) = m^2 c_2,$$

where

$$c_0 = \frac{h}{8\pi^2 c\mathrm{J}_0}, \quad c_1 = \frac{h}{8\pi^2 c\mathrm{J}_1}, \quad c_2 = c_1 - c_0, \quad c = 3\,.\,10^{10}, \quad h = 6{\cdot}55\,.\,10^{-27}.$$

We have found that the following bands all possess the same fine structure: I, II, V, VI, VIII, XI and XII. This structure corresponds to the sum of the three branches R, P, Q, when $c_0 = 8$ and $c_1 = 5$, hence $c_2 = -3$.

In fig. 5 we see how the fine band structure is distributed amongst the three branches R, P, Q. Below the three branches we give the fine band structure as calculated from the formula, with an indication of the intensities. Below this are the observed fine bands VIII with intensities. We give for all the bands a table (Table C) showing observed and calculated values and branches to which they belong. From these examples we see that the observed and calculated values agree very closely.

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* Victor Henri, 'Journ. de Phys. et le Radium,' vol. 3, p. 181 (1922).

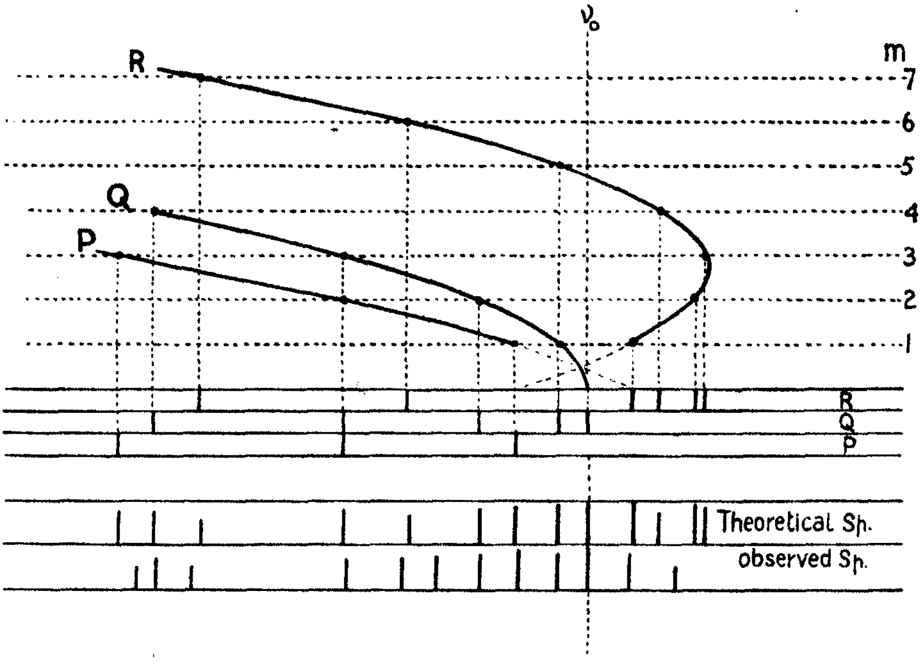

Fig. 5.

Table C.

Observed.	Calculated.	Branch.	Observed.	Calculated.	Branch.
	Band XII.			Band VIII.	
33172·3	68·5	R (3)	32464·4	63·4	R (4)
64·8	63·5	R (4)	59·3	60·4	R (1)
58·9	60·5	R (1)	55·4	55·4	Q (0)
55·5	55·5	Q (0)	52·4	52·4	Q (1)
52·5	52·5	Q (1)	47·9	47·4	P (1)
48·4	47·5	P (1)	43·5	43·4	Q (2)
45·1	43·5	Q (2)	38·0		
35·1	35·5	R (6)	34·8	35·4	R (6)
			28·2	28·4	P (2)
			23·9		
			10·7	12·4	R (7)
			05·1	07·4	Q (4)
			01·7	03·4	P (3)
			32380·4	80·4	Q (5)
			68·2	65·4	R (9)
			46·1	45·4	R (10)
			37·7	35·4	P (5)

Table C—*continued.*

Observed.	Calculated.	Branch.	Observed.	Calculated.	Branch.
	Band VI.			Band VI.	
32030·0	29·9	R (4)	31964·3	66·8	R (2)
27·2	26·9	R (1)	63·1	62·8	R (4)
21·9	21·9	Q (0)	58·7	59·8	R (1)
18·4	18·9	Q (1)	54·8	54·8	Q (0)
14·1	13·9	P (1)	52·9	51·8	Q (1)
10·9	09·9	Q (2)	46·2	46·8	P (1)
01·8	01·9	R (6)	40·9	42·8	Q (2)
31994·1	94·9	R (2)	33·8	34·8	R (6)
79·5	78·9	R (7)	28·4	27·8	P (2)
73·7	73·9	Q (4)	19·5		
70·6	69·9	P (3)	10·6	11·8	R (7)
	Band II.			Band I.	
31525·5	23·7	R (3)	31467·4	67·5	R (2)
16·4	15·7	R (1)	60·7	60·5	R (1)
10·7	10·7	Q (0)	55·5	55·5	Q (0)
08·2	07·7	Q (1)		52·5	Q (1)
04·2	02·7	P (1)	48·4	47·5	P (1)
31499·2	98·7	Q (2)	41·3	43·5	Q (2)
94·4			36·4	35·5	R (6)
89·7	90·7	R (6)	28·8	28·5	P (2)
	83·7	P (2)	20·9		
67·4	67·7	R (7)	11·8	12·5	R (7)
				07·5	Q (4)
			03·2	03·5	P (3) R (8)
			31393·0		
			79·5		
			65·4	65·5	R (9)
			54·8		
			45·4	45·5	R (10)
			34·8	35·5	P (5)
			23·8	23·5	R (11)

V.—CONCLUSIONS.

The examination of the structure of the absorption spectrum of naphthalene vapour shows that it is in fact very simple and can be accounted for on the Bohr and quantum theories. At first thought one would certainly not have expected so simple a structure in the case of a substance like naphthalene, consisting of 10 carbon atoms, 8 hydrogen atoms and 68 electrons. One would have expected a very complicated spectrum, as a result of the combined movements of all these electrons and atoms, which would be impossible to disentangle. This simple structure suggests that the atoms vibrate in a co-ordinated manner, and that it is rather groups of atoms than single ones that vibrate in the naphthalene molecule. In the case of naphthalene we have a spectrum which is entirely analogous to that of benzene vapour, which agrees very closely with the theoretical spectrum that one would expect from a large molecule built up of two groups of atoms vibrating in conjunction with each other in agreement with the quantum theory.

In the case of naphthalene we can imagine that the spectrum is caused by the vibrations of the two benzene nuclei and of the two C_3H_3 in each nucleus. We cannot allot any particular vibration to any group until we have studied the absorption spectra of other naphthalene derivatives.

A result of importance with reference to the stability of the naphthalene molecule is that after a well-marked limit of $\lambda = 2820$ representing an activation energy of 101,000 calories per gm. mol., continuous bands appear, caused by the molecule becoming more labile owing to a loosening of the bonds between the various atomic groups. Benzene vapour has been studied till $\lambda = 1900$ Å, and no change of spectrum has been observed, the bands being fine and sharp for the entire length of the spectrum. This indicates that the benzene molecule is stabler than that of naphthalene, which is in accordance with their chemical re-activity.

The existence of the three branches R (m), P (m), Q (m), accounting as they do for the fine structure of naphthalene, shows that there is a change in the moment of inertia of the molecule when excited. We have found the values 8 and 5 for the constants c_0 and c_1; hence we get the following moments of inertia :—

$$\text{For normal molecule } J_0 = \frac{h}{8\pi^2 c \,.\, 8} = \frac{6{\cdot}55 \,.\, 10^{-27}}{8\pi^2 \cdot 3 \,.\, 10^{10} \,.\, 8} = 3{\cdot}55 \,.\, 10^{-40};$$

$$\text{For excited molecule } J_1 = \frac{h}{8\pi^2 c \,.\, 5} = 5{\cdot}5 \,.\, 10^{-40}.$$

This shows that when the molecule is excited the moment of inertia increases considerably. Hence the atoms change their position when the molecule is excited.

The moment of inertia that we get for the molecule of naphthalene is much smaller than what we would expect to find for it, and than that which could be calculated from Sir William Bragg's* dimensions of the molecule. These dimensions of the naphthalene molecule have not been directly determined; Bragg has shown that in the case of naphthalene crystals entire molecules are situated at the corners of the crystal cell and the middle of the planes 001, and the dimensions have been calculated by observing the variation of the c axis as we pass from naphthalene to anthracene crystals. This axis increases by 2·5 Å; this represents according to Bragg the length of a benzene nucleus.

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[*] Sir William Bragg, 'Trans. Chem. Soc.,' vol. 121, p. 2766 (1922).

Sir W. Bragg suggests that in a molecule of benzene or naphthalene the carbon atoms are situated at distances of about the same order as in the diamond crystal (C — C = 1·54 Å) or in the graphite (C — C = 1·46 Å). This distance is determined in the carbon crystals by the magnitude of the orbits of valence electons of the carbon atom. These four valence electrons gravitate in elliptical orbits of quantum numbers 2_1; the sphere which envelops all these orbits as calculated from Bohr's theory has a diameter of 1·32 Å.

In a molecule the carbon atoms are bound together by valence electrons, whose orbits are not further apart than in the case of the atoms, but occupy symmetrical positions or envelop both atomic nuclei. The inner two electrons of a carbon atom have circular orbits of quantum numbers 1_1, their diameter being 0·18 Å. As a result, the nuclei of the carbon atoms can come much closer to each other in a molecule than in a diamond crystal. The diameter of the circular orbits of the two internal electrons of the carbon atom being 0·18 Å, this is the smallest distance that can exist between two carbon nuclei in a molecule.

If, therefore, the value for the moment of inertia found by the analysis of the vapour spectrum is correct, then we can suppose that in the molecules of naphthalene and benzene, the carbon nuclei are nearer each other than in the diamond, being at a distance of about 0·5 A, and are surrounded by a sort of electronic atmosphere. The distance between naphthalene molecules in a crystal is determined by the diameter of this atmosphere. We thus get quite a different picture of molecular structure.

This hypothesis of great atomic nuclear concentration in the molecule is supported by a whole series of measurements made by Kratzer* of the band spectra of molecules of Hg, Cd and Zn, and by Frerichs† of Cu.

In all these cases they get values for the moment of inertia of the molecules of the order of 5 to 7 . 10^{-40}, which shows that if the molecule is formed of two heavy atoms, their nuclei are very near each other in the molecule.

SUMMARY.

1. The ultra-violet absorption spectra of vapours can be divided into three groups or types, corresponding to triple, double or simple quantification of the electronic, atomic, and molecular motion.

2. There is an evolution in the absorption spectrum of a vapour on approaching the higher frequencies. For low frequencies we obtain narrow bands with

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* Kratzer, 'Annalen d. Physik,' vol. 71, p. 72 (1923).

† Frerichs, 'Z. f. Phys.,' vol. 20, p. 170 (1923).

a fine structure. After a first limit the bands become continuous without fine structure. After a second limit we get broad continuous bands. The first limit indicates an intramolecular change in the distribution of the electrons. The second limit corresponds to the ionisation of the molecule.

3. For naphthalene, the first limit of "Intramolecular loosening" corresponds to an increase of energy of 101,000 cal. gr./mol., and the second, "Ionisation of the molecule" to 230,000 cal. gr./mol.

4. The absorption spectrum of naphthalene vapour consists of two groups of bands; A from 2820 to 2500 Å of narrow continuous bands, B from 3200 to 2820 Å of narrow bands with fine structure. There are more than 400 fine bands in this group.

5. The distribution of the bands of group B can be represented by a single formula with three fundamental atomic frequencies—

$$\alpha = 474 \cdot 4, \qquad \beta = 203 \cdot 4, \qquad \gamma = 62 \cdot 7 \text{ cm.}^{-1}.$$

6. The main frequency is about half that of benzene and its mono-derivatives. It is supposed that this frequency corresponds to the vibrations of the two benzene nuclei in the molecule of naphthalene.

7. The fine structure of the bands is represented by the sum of three series, corresponding to a positive, negative and zero branch.

8. The moment of inertia of the naphthalene molecule changes on activation. The distribution of the atoms in the activated molecule is therefore different from that in the normal.

9. The numerical value of the moment of inertia of the naphthalene molecule is smaller than would be expected from the dimensions of the molecule as given by Sir William Bragg, if the distances between the carbon atoms were the same as in the diamond crystal. It is therefore supposed that in a molecule of naphthalene the nuclei of the carbon atoms are nearer each other than in a carbon crystal.

Ultra-Violet Emission Bands associated with Oxygen.

By R. C. JOHNSON, B.A., B.Sc., Lecturer in Physics, Queen's University, Belfast.

(Communicated by Prof. T. R. Merton, F.R.S.—Received April 8, 1924.)

(PLATE 7.)

OF emission band spectra generally attributed to oxygen the best known is the negative band spectrum with four strong heads at λλ6420–6300 ; λλ6010–5960 ; λλ5630–5550 ; λλ5290–5200. In addition there are several other fainter bands about λλ5900–5840 ; λλ6790–6700 ; λ6200 ; λ4980, etc. This spectrum appears with considerable intensity in the yellowish-white glow surrounding the negative electrode of a discharge tube containing pure oxygen, while at lower pressures it is visible along the capillary of the tube. The diffuse character of the bands under the dispersion of an ordinary prism spectrograph renders such wave-length determinations of little value however, except as serving for identification of the bands, and they do not appear to have been measured under high dispersion. The spectrum has been investigated by numerous observers,* and although it has not been found in absorption there is general agreement that it arises from an oxygen molecule.

In the far ultra-violet (λλ1830–1920) Schumann,† using a fluorite spectrograph, was the first to obtain emission and absorption bands of oxygen. These bands were investigated in some detail by Steubing (*loc. cit.*), who confirmed Schumann's observations and showed that the system consists of some five bands extending from λλ1831–1845 ; λλ1848–1863 ; λλ1864–1881 ; λλ1882–1899 ; λλ1900–1919. Each head consists of about eleven lines giving the appearance of being degraded to the red ; and the most refrangible head is the strongest of the five. He was also able to excite in this region the fluorescence spectrum of oxygen. It was found to coincide in position with the emission bands, though the intensity distribution in the spectrum was somewhat different. The two less refrangible heads, it should be mentioned, were observed in fluorescence only. The bands were attributed by him to an O_2 molecule and this appears to have been accepted by later workers ; though Kayser* took exception to these views.

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* Schuster, 'Proc. Roy. Soc.,' vol. 27, p. 383 (1878), and 'Phil. Trans.,' vol. 170, 1, p. 37 (1879). Croze, 'C.R.,' vol. 153, p. 664 (1911). Steubing, 'Ann. der Phys.,' vol. 33, pp. 553–584 (1910).

† 'Smithsonian Contributions to Knowledge,' 1903.

Schumann did work still further down in the ultra-violet, and this seemed to indicate a continuous absorption by oxygen below λ1850. Lyman,† however, traced the absorption band down to a maximum between λλ1400–1500, and showed that over a range of pressures from 0·02–760 mm. of mercury the band broadened almost symmetrically. This work of Schumann and Lymann points to the likelihood of there being another emission band spectrum associated with oxygen in the extreme ultra-violet.

In the paper already mentioned, Steubing expresses the view that the so-called water-vapour bands (which consist of four well-defined heads at λλ3333–3064 ; λλ3057–2811 ; λλ2806–2608 ; λλ2859–2449 ; degraded to the red) are really an oxygen spectrum. In this contention he was afterwards upheld by Stark, who ascribed them in particular to a "monatomic oxygen molecule." The weight of opinion, however, is probably against this view (*vide* Kayser,‡ Liveing and Dewar,§ and most later observers).

In Stark's paper|| a further spectrum is described and reproduced, which was considered by him to be an emission spectrum of ozone. This consists of a considerable number of well-defined heads degraded to the red and extending from about λλ2280–5000. The present communication deals with the origin of this spectrum. It has been accurately measured and the bands put into series, and the investigations made indicate that it is probably an oxygen spectrum and not an ozone emission spectrum as Stark had suggested.

Experimental.

Discharge tubes of the end-on pattern were used for the work, and the most satisfactory bore was found to be about 15 mm. The tubes were ground at the ends and fitted with quartz windows, which were fastened on by sealing-wax. Small side bulbs containing respectively caustic potash, phosphorus pentoxide, and powdered potassium permanganate, were sealed on to each tube and in addition a palladium regulator was included for the admission and removal of hydrogen. The tubes were evacuated by a Gaede rotary pump and cleaned in the usual way by the passage of a heavy current. Removal of the carbon was facilitated by the admission of small quantities

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* 'Ann. der Phys.,' vol. 34, pp. 498–504 (1911).

† 'Astrophys. Jour.,' vol. 27, 2, p. 87 (1908).

‡ *Loc. cit.*

§ 'Roy. Soc. Proc.,' vol. 43, p. 347 (1888) ; 'Phil. Trans.,' vol. 179, p. 27.

|| 'Ann. der Phys.,' vol. 43, 2, p. 319 (1914).

of oxygen obtained by gently heating the bulb containing the permanganate. The tubes were sealed off showing only the negative bands and the compound line spectrum of oxygen. Frequently, however, carbon made its appearance again, and the Ångström bands occupied the capillary, with the negative bands only faintly visible at the cathode. By running a discharge through the tube the carbon could be easily removed, being absorbed as CO_2 by the potash. If excess of oxygen was admitted, as accidentally happened on one or two occasions, this could be remedied immediately by admission of hydrogen which was removed as water by the pentoxide. When the tube was practically free from impurities, the pressure of oxygen being low, the tube glowed with a yellowish white colour along the whole length of the capillary, the negative bands of oxygen showing brilliantly. The yellowish glow was intensified by using a very mild condensed discharge, and this arrangement was adopted for photography of the band system. Photographs were taken on a large quartz-prism spectrograph having a dispersion of about 6 A per mm. at λ2300 and 16 A per mm. at λ3000. Exposures of about six hours were given. Oxygen was admitted every 20 minutes in order to maintain the pressure at its optimum value. The plate shows the spectrum in question, the only impurity being the mercury line at λ2536. Both $KMnO_4$ and $KClO_3$ were used as sources of oxygen, and there would seem to be no doubt that the spectrum arises from an oxygen molecule of some kind. Stark, in his observations, used a stream of oxygen generated from $KClO_3$ and dried over P_2O_5.

Origin of the Spectrum.

As already indicated, these bands were attributed by Stark to the ozone molecule, chiefly on the grounds of approximate coincidence of several of the strong bands with the positions of ozone absorption bands. In the region $\lambda\lambda$3220–3566 Ladenburg and Lehmann* had measured about twelve absorption bands, some of which were given to an accuracy of three figures only. From $\lambda\lambda$4330–4925 Chappuis† had recorded six absorption bands, and Schone‡ a band at λ4520. These are tabulated by Stark, and his own measurements of the emission bands to which they are assumed to correspond are recorded alongside. In the region λ3157–2710 of the spectrum, of which there was at the time no record, he photographed another ten absorption bands of ozone, and further identified these with some 21 of the emission bands which were appropriately grouped together by him. He admits that owing to the diffuse character of the absorption bands good agreement of the wave-lengths is not to be expected, but on the basis of the comparison made he attributes the whole emission band-spectrum to ozone.

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* 'Verh. d. Deutsch. Phys. Ges.,' vol. 8, p. 125 (1906).

† 'C.R.,' vol. 94, p. 858 (1882).

‡ 'Chem. News,' vol. 69, p. 219 (1894).

In addition it should be mentioned that at one time Stark was of the opinion that the negative band-spectrum of oxygen might really be part of the same ozone emission spectrum. Upon closer investigation this was not found to be tenable, but the suggestion was made that some of the fainter associated bands might possibly correspond to the strong ozone absorption bands at λλ628; λλ609–593; λλ577–560; λλ508–502. This latter must necessarily be regarded as an open question till more accurate measurements of these bands are available, though, to the writer, an examination of a strong plate of the negative band-spectrum does not seem to favour this identity.

As to the origin of the ultra-violet emission bands the writer has been led to much more definite views and holds that their identity with ozone emission bands cannot be sustained. Even if Stark's identifications were to be accepted, a number of strong heads of the same type are, according to his own wave-lengths, unaccounted for.

A more accurate measurement of the wave-lengths of the emission bands has been made by the writer (*vide* Table I). The values given represent the mean of three independent determinations, in each of which between three and six settings of the micrometer were made on each head. In some cases observation was difficult by reason of superposed band work, and this accounts adequately for any outstanding discrepancies between the observed and calculated values of the table. The more accurate measurements of the absorption bands of ozone made in 1917 by Fowler and Strutt* have been compared with the above over the range available (λλ3432–3089), and outside this range a comparison with the values of Ladenburg and Lehmann and Chappuis has further indicated that the above well-defined emission bands are not to be identified with the ozone absorption bands. During the measurements of our plates, however, a number of faint diffuse bands were recorded, apparently degraded to the red, but of a doubtful character, and a question mark was placed against these measurements at the time. Subsequently, when comparison of these wave-lengths with the absorption bands was being made, it was discovered that nearly all the bands that had been queried were close to a strong absorption band. A survey of the plate under the micrometer

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* 'Roy. Soc. Proc.,' vol. 93, p. 577 (1917).

Table I.

λ (I.A.) Obs.	Intensity.	Wave-Number in Vacuo (Obs.).	Wave-Number in Vacuo (Calc.).
4403·0	4	22707	—
4219·1	0	23696	—
4199·2	1	23809	—
4115·8	8	24292	24292
4082·4	8	24490	24492
3997·3	4	25011	—
3959·4	6	25251	—
3950·6	6	25307	—
3929·0	7	25446	—
3859·5	8	25904	25901
3830·5	8	26100	26101
3733·9	8	26776	26770
3727·5	8*a*	26822	26849
3706·6	8	26974	26970
3701·2	8	27013	—
3629·8	8	27543	27545
3620·1	2	27617	27613
3603·7	7	27744	27745
3594·5	2	27813	27813
3517·7	8	28423	28414
3494·2	7	28611	28614
3421·2	8	29222	29223
3416·2	2	29266	29256
3397·8	8	29422	29423
3393·1	4	29463	29456
3322·6	6	30089	30092
3300·3	6	30293	30292
3231·2	8	30941	30934
3210·8	8	31137	31134
3141·0	5	31829	31803
3123·1	5	32012	32003
3062·8	8	32642	32645
3043·6	8	32848	32845
2987·5	8	32461	33461
2970·0	7	33660	33661
2961·5	4	33757	33748
2952·5	5	33860	—
2937·1	2	34041	—
2919·8	8	34250	34250
2907·1	5	34393	34390
2901·9	7	34453	34450
2895·6	8	34524	—
2890·3	7	34590	34590
2881·8	6	34691	—
2876·6	5	34753	—
2861·0	3	34944	—
2839·7	9	35206	35206
2823·7	8	35407	35406
2806·1	3	35630	—
2776·7	7	36003	35995
2761·9	7	36198	36195
2720·0	7	36756	36757
2705·3	7	36958	36957
2688·5	2	37182	37185
2666·5	4	37491	37493
2652·3	4	37693	37693

a = confused with a line.

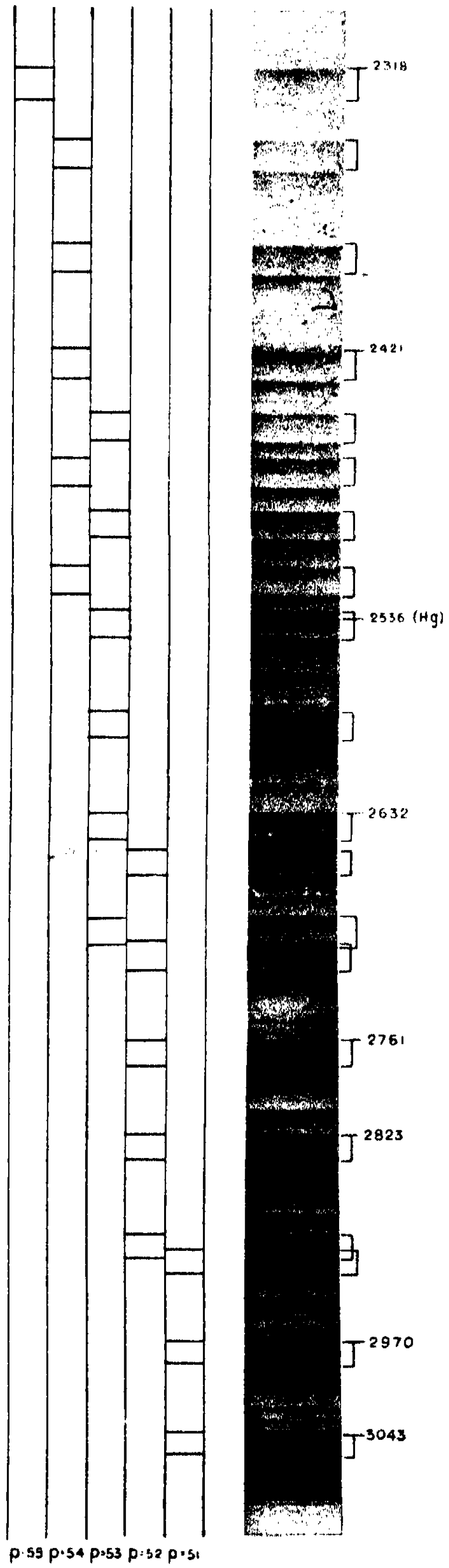
Table I—*continued*.

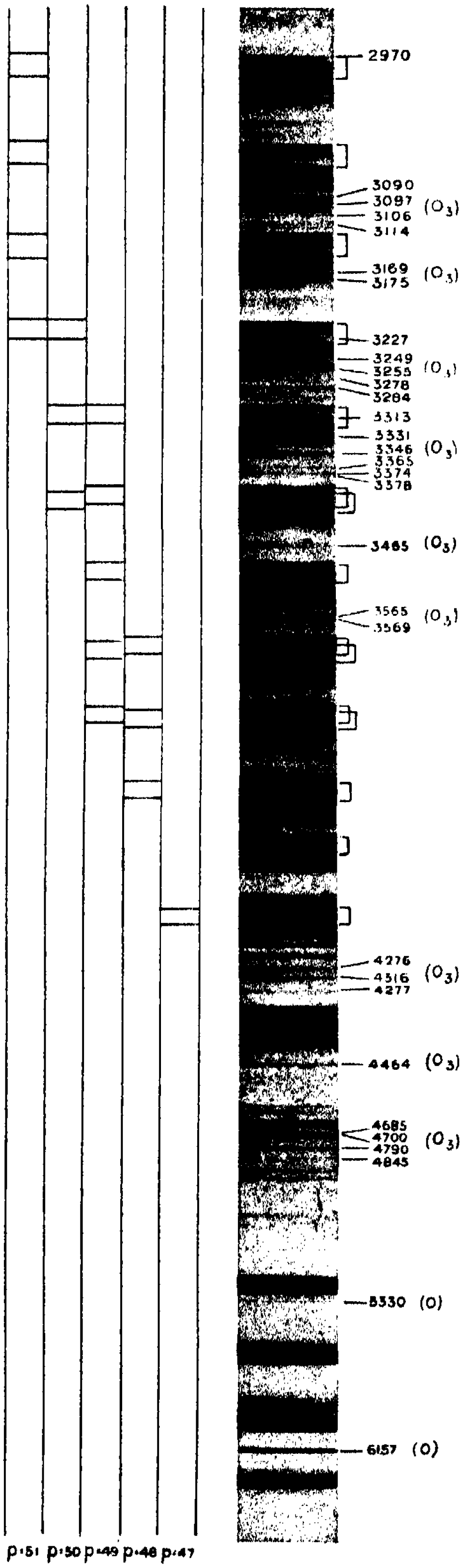
λ (I.A.) Obs.	Intensity.	Wave-Number in Vacuo (Obs.).	Wave-Number in Vacuo (Calc.).
2646·7	6	37773	37774
2632·7	6	37974	37974
2594·3	8	38533	38536
2488·4	1	38620	—
2581·0	8	38734	38736
2545·5	7	39275	39272
2532·8	6	39472	39472
[2512·9	3	39785	39787
2500·6	6	39980	39980
2488·3	6	40175	40180
2478·0	4	40342	40349
2465·8	2	40543	40549
2458·6	1	40663	40662
2446·9	1	40859	40862
2433·5	3	41083	41085
2421·8	2	41282	41285
2392·6	3	41783	41793
2381·0	3	41988	41993
[2376·4	1*b*	42067	42018
2354·3	1	42464	42475
2343·3	1	42665	42675
[2318·7	1	43120	43127

b = faint and diffuse.

Table II.

Ozone Absorption Bands.	Emission Bands.	Ozone Absorption Bands.	Emission Bands.
4845	Visible.	3311·5 5	3313·1 5
4790		3304·1 3	Conf. with band.
4700	Visible.	3284·0 2	3284·6 2
4685		3279·8 8	3278·1 2
4645	Visible.	3272·0 3	Faintly visible.
460		3255·5 5	Visible.
452	—	3249·7 8	Visible.
4465	4464·7 1	3243 1	—
444	—	3232·8 1	Conf. with band.
433	4333·3 2	3227·2 10	Doubtful, conf. with band.
	4316·5 5	3221·5 10	
	4276·9 2	3206·8 2	Visible.
3566	3568·9 2	3201·0 8	Visible.
	3565·2 1	3194·8 6	Visible.
3503	—	3188·8 1	Visible.
346	3465·3 0	3181·5 1	—
3432·2 1	—	3177·0 8	3175·0 Conf.
3421·4 1	—	3171·6 4	3169·5 Conf.
3402·6 1	—	3162·6 2	—
3377·7 1	Visible.	3156·1 8	Conf. with band.
3374·1 3	3378·3 1	3137·4 10	Visible.
3365·2 1	Visible.	3114·3 8	Conf. with band.
3346·0 1	—	3105·0 5	3106·1 5
3338·5 4	3337·8 6	3096·5 4	3097·5 4
3331·2 1	3331·5 4	3089·5 8	3090·4 8


2318
2421
2536 (Hg)
2632
2761
2823
2970
3043
p·55 p·54 p·53 p·52 p·51


2970
3090
3097
3106
3114
(O3)
3169
3175
(O3)
3227
3249
3255
3278
3284
(O3)
3313
3331
3346
3365
3374
3378
(O3)
3465 (O3)
3565
3569
(O3)
4276
4316
4277
(O3)
4464 (O3)
4685
4700
4790
4845
(O3)
5330 (O)
6157 (O)
p·51 p·50 p·49 p·48 p·47

was therefore made, in a search for faint emission bands where known absorption bands existed, and Table II shows the result of this search from λ3089 upwards.

The fact that more of these true ozone emission bands were not recorded when the plate was measured is accounted for by the faintness of the bands, which were therefore easily confused with the fine structure of the main emission bands. The position of those which are visible on the negative is indicated on the plate reproduced. Of course this does not prove conclusively that the main ultra-violet bands are not due to ozone: but if they are, it is at least contended that there is no corresponding absorption spectrum known.

The main band system has been found to fall almost completely into nine series, the intensities of the members visible in any one series being low for the extreme members and rising to a maximum for the central members. The series are shown diagrammatically on Plate 7. Any one series can be obtained from any other by displacement of its members through a constant amount. The corresponding members of different series also obey the band series law so that the whole band system can be expressed by a Deslandres formula of the type:—

$$\nu = \mathrm{A} + \mathrm{B}p^2 - \mathrm{C}m^2.$$

The system is found to be well represented by:—

$$\nu = \left.\begin{matrix}1620\\1420\end{matrix}\right\} + 16 \cdot 945\, p^2 - 13 \cdot 37\, m^2.$$

This arrangement into series is shown in Table III. The bands are found to go in pairs, having a wave-number interval of 200 units. In the table the more refrangible head alone is indicated, for the sake of simplicity. With p constant and successive integral values given to m a column is traversed; with m constant and successive integral values given to p a row is traversed. Other well-known spectra which have been arranged into similar series are the 1st positive bands of nitrogen by Cuthbertson[*] and Deslandres[†] and the less refrangible spectrum of cyanogen by Fowler and Shaw.[‡]

The fact that most of the strong emission bands of the spectrum fit naturally into the formula, and that none of the faint diffuse bands identical with the ozone absorption bands do so, seems clearly to indicate another molecular origin. Some clue to the nature of the radiating molecule might conceivably be obtained on the basis of the quantum theory if a simple numerical relation

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[*] 'Phil. Mag.,' vol. 6, 3, p. 348 (1902).

[†] 'C.R.,' vol. 134, p. 747 (1902).

[‡] 'Roy. Soc. Proc.,' A, vol. 86, p. 118 (1912).

Table III.

p	55		54		53		52		51		50		49		48		47
m																	
25			42665	*1807*	40859												
			677		*684*												
26			41988	*1813*	40175												
			706		*703*												
27	43120	*1842*	41282	*1810*	39472	*1779*	37693										
			739		*738*		*735*										
28			40543	*1809*	38734	*1776*	36958										
			758		*760*		*760*										
29			39785	*1811*	37974	*1776*	36198	*1745*	34453								
					792		*791*		*791*								
30					37182	*1775*	35407	*1747*	33660		Obsc. by OH band.		30293				
							817		*812*				*830*				
31							34590	*1742*	32848	*1711*	near 31137	*1674*	29463	*1650*	27813		
									836		*844*		*852*		*839*		
32									32012	*1719*	30293	*1682*	28611	*1637*	26974		
									875		*871*		*867*		*874*		
33									31137	*1715*	29422	*1678*	27744	*1644*	26100	*1610*	24490
													922				
34													26822				

Other heads are 200 units less than the above.

were found to exist between the second-order differences 33·89, 26·74, and the second-order difference of, say, the negative band spectrum. The fine structure of the latter, however, is not known with sufficient accuracy to furnish any evidence. It is therefore premature to suggest what oxygen molecule is responsible for the radiation.

I wish in conclusion to thank Mr. W. H. B. Cameron and Miss. M. Hall for valuable assistance, also my colleague Mr. J. Wylie for many excellent suggestions in connection with the design and construction of the spectrograph with which this work was done. Mr. Buick executed these plans with great skill.

Finally I am much indebted to the kindness of Prof. W. B. Morton, whose constant interest in the work I have appreciated, and to Prof. T. R. Merton for helpful advice in connection with the drafting of the paper.

A Method of Producing Strong Magnetic Fields.

By P. L. Kapitza.

(Communicated by Prof. Sir E. Rutherford, F.R.S.—Received April 9th, 1924.)

(From the Cavendish Laboratory, Cambridge.)

[Plate 8.]

Introduction.

There are only two methods of producing a strong magnetic field. The first is by a solenoid, and the second by a solenoid with an iron core in it. The iron is introduced for the purpose of diminishing the magnetic resistance of the magnetic flux, and makes possible the production of much stronger fields than can be obtained without it. This is the principle on which modern electro-magnets are constructed, and by means of them it is possible to obtain fields up to 60 kilogauss in a volume of a few cubic millimetres. The saturation of iron, however, makes it impossible to go further than this.

According to the present theory of ferro-magnetism we can hardly hope to obtain any ferro-magnetic material which will give a much higher saturation-value than the iron used in modern electro-magnets; and without such a material it is impossible to increase the field obtainable by this means.

With an uncored solenoid we are limited for producing magnetic fields by two factors: (1) the very powerful sources of electric energy which are needed, and (2) the necessity of avoiding over-heating of the coil. On account of these limitations it is difficult to obtain in this way fields of more than 15 to 20 kilogauss, even if extremely powerful sources of energy are used and very efficient cooling of the solenoid is arranged.

To Perrin is due the idea of cooling the coil with liquid air. This clearly would not only very efficiently avoid over-heating, but also, since at low temperatures the conductivity of copper is considerably increased, would diminish the power required. But Fabry* has calculated that to obtain 100 kilogauss in a coil of one centimetre inside diameter, 24 litres of liquid air per second would be necessary, with a source of energy of 400 kilowatts. Thus the experiment is scarcely a possible one. So it seems hopeless to obtain a strong magnetic field by any of the usual methods.

There appears to be only one possibility, which is to produce the magnetic field for only a very small time (say of the order of one-hundredth of a second). In this case the difficulty with the heating is at once reduced. Nearly all the phenomena, which are interesting to study, such as, for instance, magneto-optics, para- and dia-magnetism, and other effects of atomic origin, will exhibit themselves in this short-lived field just as well as in a permanent field. The methods of observing the effects in this case will be quite different from the usual ones, and also, possibly, in some cases the difficulties of observation may be insuperable. But we may hope that it will still be possible to make observations in many cases in spite of the shortness of the time, especially in view of the fact that, in strong fields, the scale of the effects will be increased and observation will therefore be easier.

If we wish to experiment with strong fields, then we have to meet the difficulties involved in the use of fields of short duration. The present paper contains an account of a method for obtaining magnetic fields of short duration, of strength up to 500 kilogauss. This method has already been applied for bending the α-ray tracks in a Wilson expansion chamber, but in view of the general interest of the method of producing the fields, we shall reserve the details of these α-ray experiments for a later paper.†

In the development of the method four separate problems had to be solved, and to each of these a separate section will be devoted. The first is the powerful source of energy, the second the switches and connections necessary

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[*] Fabry, 'Journal de Physique,' ser. 4, vol. 9, p. 129 (1910).

[†] For a preliminary account of these α-ray experiments see 'Proc. Cambs. Phil. Soc.,' vol. 21, p. 511 (1923).

for dealing with the high currents involved, the third the accurate measurement by means of oscillographs of these heavy currents, and the fourth the calculation and construction of the most efficient type of coils for producing the field.

§ 1. *Sources of Energy.*

The power necessary to produce a magnetic field increases as the square of the field strength required. In the present experiments sources of energy up to 1,200 kilowatts are needed. Such a power is obtainable by means of a large plant of electro-generators of the usual type, but this would scarcely be available for ordinary laboratory work. Also, it is obvious that since the energy is required for only a small fraction of a second, a source of different type might be more suitable. In fact, any apparatus capable of storing energy during a considerable period and of letting it loose in a small fraction of a second could be employed for the production of intense magnetic fields.

There are two quantities which are characteristic of such a source of energy: (1) the total energy stored, needed for the production of the field, which in our experiments reached the value of 2·5 great calories; and (2) the ratio of the power, by means of which the apparatus is charged, to the power at which it is discharged.

This quantity we shall call the coefficient of the power increase, and the larger it is, the more suitable is the source of energy. The methods of producing such a store are numerous, but we shall consider only the principal ones. A condenser battery is the most obvious. Its coefficient of power increase is probably larger than in any other kind of apparatus, but the main objection against its use, as can be seen from a rough calculation, is the difficulty of storing a considerable amount of energy. Very high tension and very large capacity are necessary. For instance, to obtain 2·5 great calories a condenser battery about 20 microfarads charged to 50 kilovolts is required.

Another method, which looked more promising at first sight, is to store the energy magnetically. A simple iron core, as used in induction coils, stores magnetic energy when magnetised by the current in the primary. Breaking the current in the primary, this energy of the iron core is transferred to the current in the secondary. Using in the secondary winding only a few turns, it would be possible to obtain strong currents capable of producing powerful magnetic fields. Calculation shows that an iron core 2 or 3 metres long and 30 to 40 cm. diameter, will yield quite sufficient energy, and the coefficient of power increase will be of quite a reasonable magnitude.

This method was actually tried by Mr. P. M. S. Blackett and the present author on a small scale, but we met with practical difficulties which made its application very difficult. In practice it was impossible to break the primary sufficiently quickly to prevent sparking, and the energy of the magnetised iron core, instead of going into the secondary, returned through the spark into the main circuit of the primary. Calculation shows that the tension in the break of the primary was very high, and probably no mechanical break would work satisfactorily. The introduction of a condenser in the usual way will reduce the spark, but will also considerably decrease the coefficient of power increase.

It is also possible to accumulate energy mechanically. For instance, if we have a very quickly spinning fly-wheel connected with an electro-generator of a special type, then large power could be obtained by suddenly switching in the latter on a small resistance. Probably we might get a power 30 to 50 times as large as that given by a generator of similar size in continuous running. It is probable that this method would work quite satisfactorily, but as it requires a specially built generator, to run at a very high speed and with a special winding, a considerable expense is involved.

The method which was actually used has given quite satisfactory results and is probably the cheapest and simplest. We stored the energy chemically. An accumulator was constructed of a very small capacity, small resistance and of a rigid design, suitable for standing sudden discharges.

In fig. 1 a sketch is given of one of the four batteries used. Its construction is extremely simple. Lead plates, 35 cm. by 35 cm. and 1·5 mm.

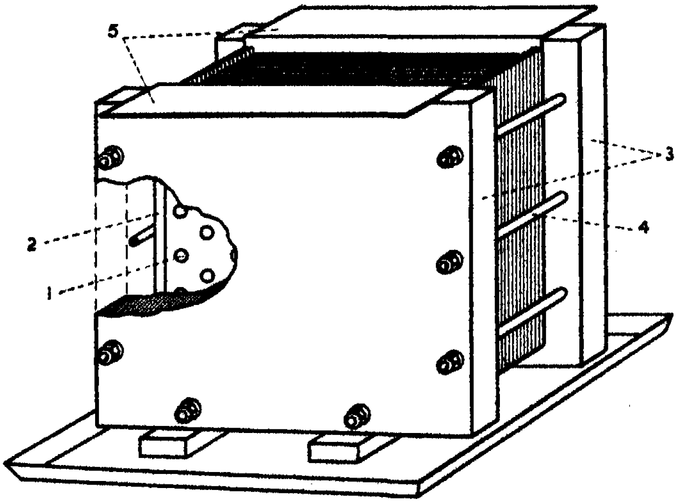

Fig. 1.

thick, were gathered into a pile. The plates were separated from each other by 30 india-rubber discs, 1·5 cm. diameter and 1·7 mm. thick, which were placed in a regular way between the plates. In fig. 1, where the section is made on the left-hand side of the drawing, these discs (1) are shown as circles. They are stuck to one of each pair of plates by means of india-rubber solution. The edges of the plates are separated by means of rubber washers (2), which have a U shape and cover the plates on the edges in such a way as to make a receptacle for acid between each pair of plates. The whole pile contained 71 plates and was fastened between two solid slate slabs (3), which are held together by means of eight bolts (4), thus providing a water-tight joint between the pairs of rubber washers. The two end-plates (5) were of thick lead and projected out of the pile to provide terminals on to which to connect the cables. The slate-plates and the bolts were covered with tar-varnish to prevent them from being attacked by the acid. Each gap between the plates was filled with 30 per cent. solution of sulphuric acid to 0·9 of its height. The current flowed between the terminals and passed successively through all the gaps. The plate on one side of a gap was charged positively and on the other negatively in such a way that each gap formed a separate cell connected in series with the others forming the battery.

Such a battery obviously has an extremely small internal resistance on account of the thin layers of acid and of the fact that the current between two successive cells flows across the lead sheets. Its capacity is also very small on account of the thinness of the active layer formed on the surface of the plates. Each of these batteries had initially a resistance of about 0·02 ohm. Four of them were made and were charged in parallel from a source of 220 volts at a current of 2 to 3 amperes. For the discharge, they were connected in two groups, each containing two in parallel, and the groups were connected in series. Discharging the whole through a resistance of 0·02 ohm, a power of over 1,000 kilowatts in the circuit can be obtained. The coefficient of power increase was well over 2,000. The current in the most efficient discharge was about 7,000 amperes, and by short-circuiting the accumulator can be made to reach 13,000 to 14,000 amperes.

Before going on to give some hints on handling these batteries, we shall state the results of measurements of the power obtained from them by their discharge through different resistances. In fig. 2 are shown charts obtained by means of an oscillograph, which will be described in one of the following Sections (§ 3). The scale on the vertical axis gives the power in kilowatts, and that on the horizontal axis the time in hundredths of a second. The different curves show the power yielded by the accumulator in discharging through different resistances between 0·055 to 0·01 ohm. It is seen that the maximum power is reached when the external resistance is equal to 0·025 ohm. In a hundredth of a second the power drops from 970 kilowatts to 480 kilowatts.

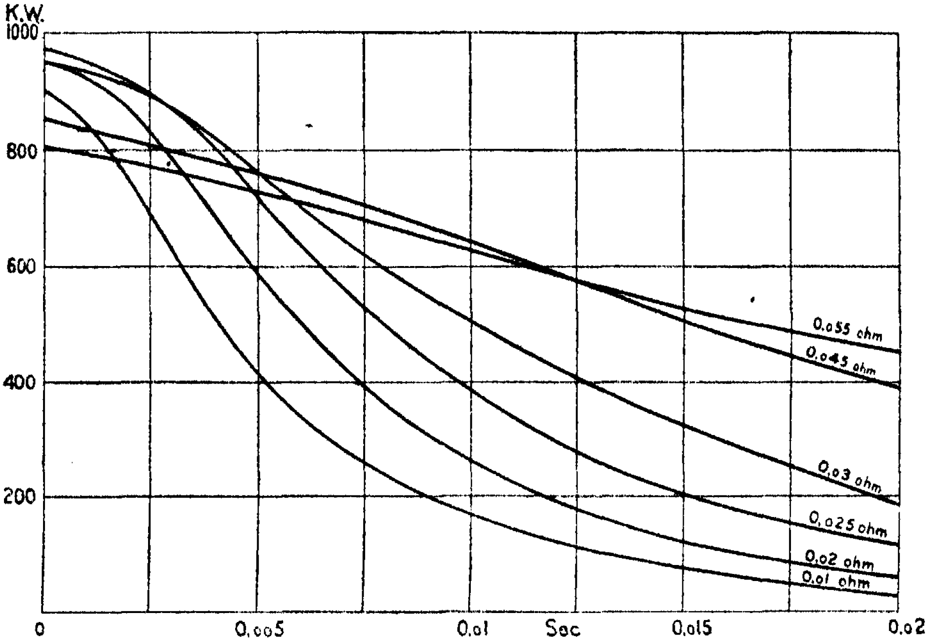

Fig. 2.

Using smaller resistances than 0·025 ohm, less power is obtained and it drops down much more quickly. For these reasons their use is valueless unless a very high current is needed ; for instance, for fusing wires. On the other hand, discharging the accumulator through higher resistances than 0·025 ohm, the power drops much more slowly with the time. This indicates that if magnetic fields of longer duration are required, resistances higher than 0·025 ohm can be used, but in this case the power will not be so great as with a resistance of 0·025 ohm.

The accumulator battery has now been in continuous use for one year. During this time the power obtained from the battery gradually diminished, and at the end of the period it had dropped from 1,200 kilowatts to 700 kilowatts. This is probably explained by the gradual increase of the positive active layer on the lead plates, causing an increase in the internal resistance. The capacity also increased ; this was easily seen from the fact that the time for charging the cells after a complete discharge was at the beginning only 2 or 3 minutes, but in a year's time extended to 15 to 20 minutes. After noticing this peculiarity of the accumulator, precautions were taken to stop it.

In the first eight months of work we used the following arrangement for interrupting the current to prevent over-heating the coil. After one or two hundredths of a second the accumulator was simply short-circuited by means of a special switch. This was a very simple method of interrupting a current of 6,000 or 7,000 amperes, but it led to the complete discharge of the accumulator every time, and the latter had to be re-charged from the beginning. This treatment helped to form the active layer. It was therefore decided to work out a method of interrupting the current, which will be described in the next section. In this way in a discharge only the surface of the active layer on the plates is involved, and probably the increase of capacity will be stopped. To verify this point finally, however, more time is needed.

The most annoying characteristic so far found in the work on the accumulator is the bursting of the lead plates. Suddenly two or three cells in a battery will cease to show any difference of potential. They also begin to heat up, and during the discharge acid splashes out of them. When the accumulator is taken to pieces, we find in the plates which form the defective cells irregularly shaped holes of about 1 or 2 cm. in diameter. From the edges of such holes, it was easily seen that the plates were burned through. The reason for this breakdown was extremely puzzling, and from a very careful study of the behaviour of the accumulator we can only suggest the most probable explanation.

The active layer of the positive plates increases in thickness with the time ; eventually some parts of it may break off and connect to the opposite plate. Cells in which this has happened are discharging themselves continuously and become much less efficiently charged than the cells in a normal state, because a considerable part of the charging current passes through the place of contact. But such a defective cell, which is easily detected by its low voltage, is not necessarily burned through unless it remain a considerable time (several days) in such an abnormal condition in a discharged state. The positive active layer then begins to get sulphated ; this means that the resistance of this cell is very much increased, and in discharging the accumulator this defective cell will absorb a large amount of energy. All the current will pass in few places where, owing to some such cause as the breaking of the active layer, the plates are locally not so badly sulphated. In these places the current density is so large that it fuses the lead.

In general, owing to the small capacity of the battery and the necessity of keeping a very small internal resistance, sulphating is much more troublesome than in an accumulator of the usual type. If the battery merely remains discharged for three days its resistance is so much increased that in the discharge only a quarter of the actual power is obtained, and only after several discharges does the accumulator regain it. Thus it is extremely important to keep the battery always charged up.

Owing to its small capacity the self-discharge of the battery is quite rapid. To make the rate as small as possible it is necessary to use chemically pure lead. Also, since the dirt lying on the bottom increases the self-discharge rate, it is essential to overhaul it, thoroughly cleaning and washing it every five or six months. With proper treatment the battery will probably stand several years of continuous work. Even in our case, where the battery was rather badly treated, the thickness of the lead plates had only diminished by $\frac{1}{10}$th mm. in a year. However, after one year the india-rubber washers were rather badly deteriorated and had to be replaced by new ones.

§ 2. *The Switch Gear.*

The problem of switching a current of the order of 10,000 amperes in a time very small compared with a hundredth of a second, during which all the experiments in the magnetic field have to be performed, must be solved by means of a special switch. The drawing of such a switch is given in fig. 3.

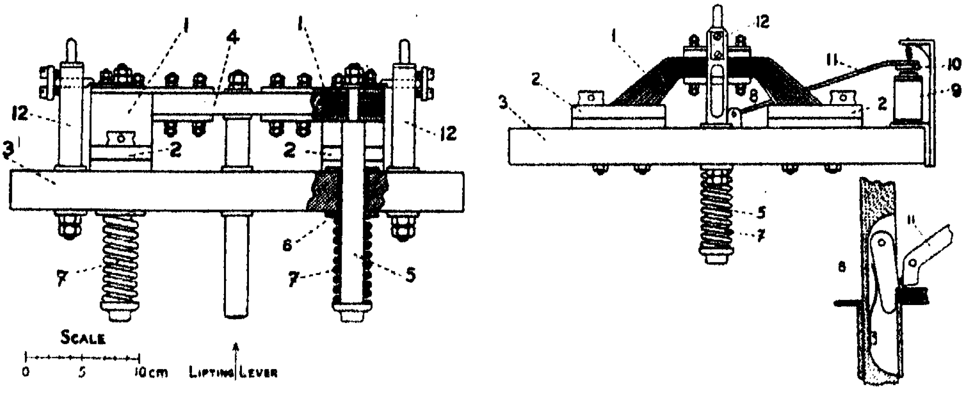

FIG. 3.

Its construction was worked out by Mr. E. I. Laurmann. It consists of two brushes (1–1) which are made from 20 separate plates of hard-drawn copper, bent in the shape shown in fig. 3 and bolted together. These two brushes, when down, rest on four copper plates (2) fixed to a solid slate slab (3), and are ground to these plates. The two brushes are joined together by means of a fibre plate (4), and through each of them a brass rod (5) passes, and these rods serve to guide the vertical motion of the brushes by sliding in two brass tubes (6) fixed in the slate. Two heavy springs (7) press the brushes towards the copper plates (2). A third brass rod, which is fastened in the middle of the fibre joint (4), bears a trigger arrangement (8) (shown separately), which keeps the brushes from falling down when they are in the raised position. This trigger can be released by means of an electro-magnet (9), which pulls down an iron plate (10) fastened to a lever (11). When released, the brushes will fall on the copper plates and close the circuit. One pair of the copper plates is connected to the battery, the other to the coil. The time of fall is about 0·025 sec. and the height of fall 3·5 cm. To prevent the brushes from jumping after the make, two catches (12) are arranged. The total resistance of the switch was less than 0·00015 ohm.

For re-breaking the current after a time of contact of the order of $\frac{1}{100}$th sec., another set of switches was constructed. It is very difficult to break a current of several thousand amperes quickly by means of a switch, but this can be done by means of a fuse. After trying different kinds of fuses, we found that the sharpest break is obtained with a copper wire. On the oscillogram No. 1 is shown the fusing of a copper wire of 0·76 mm.^{2} cross-section and 2·5 cm. length ; it is seen that the complete interruption of the current occurs in less than a hundredth of a second. The arrangement for fusing the wire is shown in fig. 4. The wire (1) rests on two copper rectangles (2) and is clamped between the terminals (3). As the copper wire fuses only between the edges of the copper rectangles, the terminals are not burned. But such a fuse, simply introduced in the main circuit, would cause the interval of time between the make and break to be badly defined. Also the wire of the fuse will contribute an appreciable resistance to the circuit. The avoid this the following arrangement was used in the main circuit :—

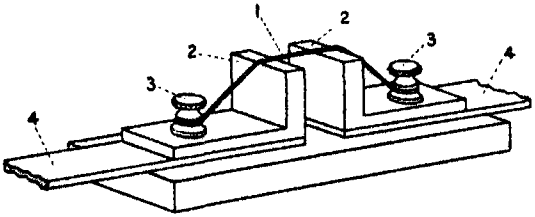

FIG. 4.

Another switch of the type just described was constructed. It was somewhat smaller and consisted only of one brush. The spring in this brush was arranged in such a way as to pull it from the contacts, and when pressed on the copper plates it was held down by means of a trigger. Releasing the trigger, the brush was thrown off and the main circuit broken. The copper leads (4) of the fuse, for which a thin copper wire was now used, were connected to the copper plates of this switch. Thus, when the latter was released, all the current, instead of flowing through the switch, which was of much smaller resistance than the fuse, began to flow through the copper wire. The rise of potential on the terminals of the switch during the break was quite small, and no arcing took place during the break. The moment of operating the break was under control, and so it was possible to regulate the moment of breaking the current. But using this scheme, it was possible to break the current only in a non-inductive circuit. If the accumulators were discharged through a coil, then a big arc occurred between the rectangles of the fuse-holder. To avoid this, another switch was introduced to short-circuit the coil just before the fuse was introduced in the circuit.

For the timing of the switches one after the other, the following arrangement was adopted : The making switch of fig 3, when falling, on its way released the trigger of the switch which short-circuited the coil, and this one operated the trigger of the switch which introduced the fuse. The place at which the big switch operated the short-circuiting switch could be adjusted, and this allowed control of the interval of time during which the tension was applied to the coil. This arrangement provided a very accurate way of timing, because the time of the fall of the making switch was only $\frac{1}{40}$th sec., and the accuracy of the timing could be adjusted to a small fraction of this time. The time of the falling of the switch was found extremely constant, so with this arrangement in practice the timing, once adjusted, kept constant to $\frac{1}{10000}$th sec. However, all the triggers should be made of hardened steel and the break carefully constructed.

The other switches used for charging the battery in parallel and discharging in groups and series were the ordinary switches designed for a continuous current of 200 amperes. For the connecting wire in the discharge circuit, a flexible cable, which consisted of 817 small wires wound together, of a total area of 130 mm.^{2}, was used. The contacts and connections were made carefully and accurately, and the resistance was occasionally measured on a Thomson bridge. The total resistance of all the switches and cables together was about 0·0016 ohm. The loss of energy in the circuit was about 7 per cent. of the total energy obtained.

§ 3. *The Method of Measuring the Current.*

The measurement of the current through the coil was made by means of an oscillograph connected to a shunt. The tension across the coil was measured by means of another oscillograph connected through a resistance of 300 ohms. The oscillograms were taken on a falling plate by the usual method, only, in our case, it was necessary to time the moment, during the time taken by the plate to pass across the slit, at which the light from the oscillograph mirror fell, relative to the moment at which the make of the current took place. This timing was arranged in the following manner: The plate, falling on its way to the slit, operated a little switch, which made the current through the electro-magnet (9) of the switch (fig. 3). The moment at which the falling plate operates the little switch is adjustable, and the timing was quite easily obtained. The plate passed near the slit with a fairly constant velocity of 1·6 to 1·85 metres per second.

The oscillographs used were of the Duddell type, but specially designed for the present experiment, since oscillographs of higher frequency (20,000 to 30,000 per sec.) than ordinarily used are required. At such high frequencies the oscillograph is very insensitive, since the sensitivity decreases inversely as the square of the frequency; but we possess such a large power that one or two amperes let pass through the oscillograph did not appreciably affect the current in the main circuit.

These oscillographs, being so insensitive, could not stand the considerable current required to produce a deflection for a time of several seconds' duration. The loop would be over-heated and even burnt. But in our case, as it was used only for a small fraction of a second, we were not troubled by this. In calibrating the oscillographs over-heating began to be appreciable, but could be easily overcome in a way described later.

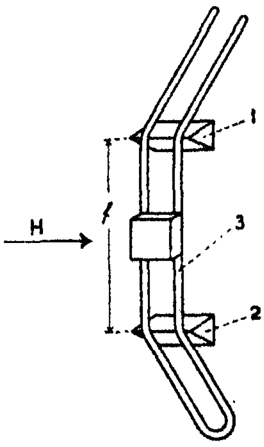

FIG. 5.

In designing this oscillograph it is important to use wire of the proper dimensions for the loop and of the mirror. In fig. 5 a diagram of the oscillograph is drawn. Between two bridges (1–2) the loop (3) is placed; it consists of bronze wire stretched by means of a spring. On the middle of the wires of the loop, between the bridges, a small square mirror, cut from a cover-glass, is fastened by means of shellac. This mirror fits exactly between the wires.

Let T be the tension on the wires,
f the distance between the bridges,
H the magnetic field,
Δ the distance through which the edge of the wire moves when a unit current is passed through the loop.

Then

$$\Delta = \frac{f^2}{T} H. \tag{1}$$

Δ is thus a measure of the sensitivity of the oscillograph.

The natural frequency of the loop can be calculated with an approximation quite sufficient for practical purposes if we assume that the half of the mass of the wire is concentrated on the point where the mirror is attached.*

If we call the mass of the wire per unit length ρ, the mass of the mirror M, and the frequency n, then

$$n = \sqrt{\frac{T}{f\left(\frac{\rho f}{2} + \frac{M}{6}\right)}}. \tag{2}$$

The tension T depends on the size of the wire. In practice, it is important, in order to obtain constant readings, to work with a tension which does not strain the wire above its elastic limit. Obviously, this tension is proportional to the cross-section of the wire, and we shall have

$$T = K\rho \tag{3}$$

where K is a constant for the material used. Since the minimum size of the mirror (about 1 or 2 square millimetres) is fixed by the necessity of obtaining a good spot of light, the frequency n is also given, so that only f and ρ can be varied. From (1), (2) and (3) we obtain

$$\Delta = \frac{\sqrt{K}}{n^3} \sqrt{\frac{\rho f}{\left(\frac{\rho f}{2} + \frac{M}{6}\right)^3}} H. \tag{4}$$

To obtain the maximum sensitivity we have, as can be easily found by differentiating the expression (4),

$$\rho f = \frac{M}{6}. \tag{5}$$

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* The formula (2) gives a maximum error of 10 per cent. from the true value if the weight of the mirror is very small compared with the weight of the wires (see Lord Rayleigh, 'Theory of Sound,' vol. 1, ch. 6).

This means that the oscillograph has a maximum sensitivity when the weight of the mirror is six times as great as the weight of a single wire between the bridges. In practice it is advisable to make the mirror lighter than is indicated by formula (5), because the oscillograph is immersed in castor oil to provide critical damping, and since the mirror will move the oil, its effective mass will be increased. From the expressions (3), (4) and (6) we obtain :

$$n = \frac{1}{f}\sqrt{\frac{2}{3}\mathrm{K}}. \tag{6}$$

From this expression we see that the frequency of an oscillograph working at the maximum sensitivity depends only on the distance between the bridges. Thus, to obtain an oscillograph of high frequency, f must be made small. In our case f was 9 mm. and the wires were of diameter 0·07 mm.

In the circuit of the oscillograph which measures the tension was introduced a non-inductivity wound coil of resistance 300 ohms. The oscillograph which measured the current was connected to a shunt of a special type. The shunting of the oscillograph in our case is somewhat difficult, owing to the fact that the current is varying. The self-inductance of the shunt L and the self-inductance of the oscillograph l may affect the distribution of the current. If we suppose I and i to be the currents in the shunt and the oscillograph and R and r to be the respective resistances, then the distribution of the currents may be obtained from the following expression :

$$ir + l\frac{di}{dt} = \mathrm{IR} + \mathrm{L}\frac{d\mathrm{I}}{dt}. \tag{7}$$

If we adjust the resistances and the self-inductances in such a way that

$$\frac{r}{l} = \frac{\mathrm{R}}{\mathrm{L}}, \tag{8}$$

then it is easily proved from (7) that the current i in the oscillograph will vary in exactly the same way as the current I. In fact

$$i = \frac{\mathrm{R}}{r}\mathrm{I}. \tag{9}$$

In our case we obtained the same result in a different way. The shunt had a very small self-inductance, thus making the term $\mathrm{L}\frac{d\mathrm{T}}{dt}$ on the right-hand side of the expression (7) small compared with the first term. If, now, a non-inductive resistance is introduced in series with the loop (which itself had a small self-induction), the term $l\frac{di}{dt}$ on the left-hand side of the expression (7) will also be small compared with ir. In such a way the condition (9) was obtained without adjusting the self-inductions.

The construction of the non-inductive shunt is shown in fig. 6. It consists of two copper rectangles (1) to which the terminals of the main cable are fastened by means of two bolts (2). The leads from the oscillograph are connected to the terminals (3). The shunt consists of constantan wires (4) bent in U shape and soldered on both sides of the rectangles, as shown in fig. 6.

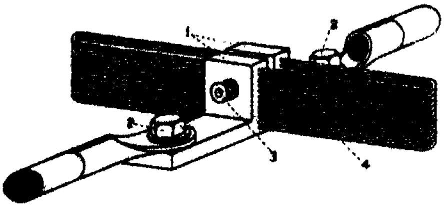


FIG. 6.

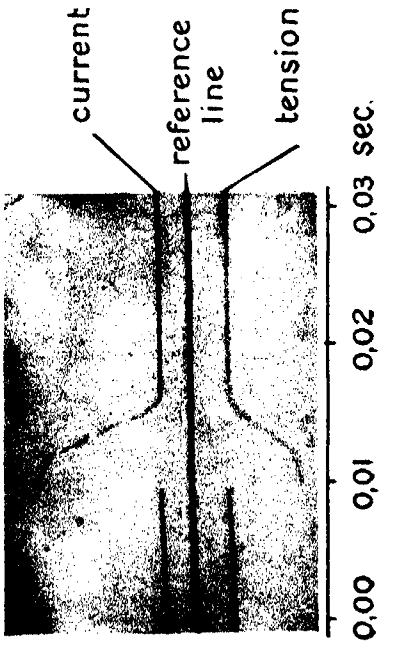
The distance between the copper rectangles is only 1 mm. The resistance of the shunt was 0·000465 ohm, and the resistance of the oscillograph circuit was 3·754 ohms.

The fact that the self-inductance did not affect the distribution of the current can easily be seen on any oscillogram of the discharge of the accumulator through a non-inductive resistance, such as, for instance, the oscillogram No. 1 (Plate 8), which is of the fusing of a wire in series with a non-inductive resistance of 0·025 ohm. On this oscillogram it can be seen that the current reaches a steady value almost at once. If L were appreciable, the curve would rise sharply to a value higher than the steady value to which it finally attains. On the other hand, if l were appreciable, no sharp break at all would be found in the curve. Oscillograms of this kind were actually obtained if a straight wire instead of the shunt (fig. 6) was used.

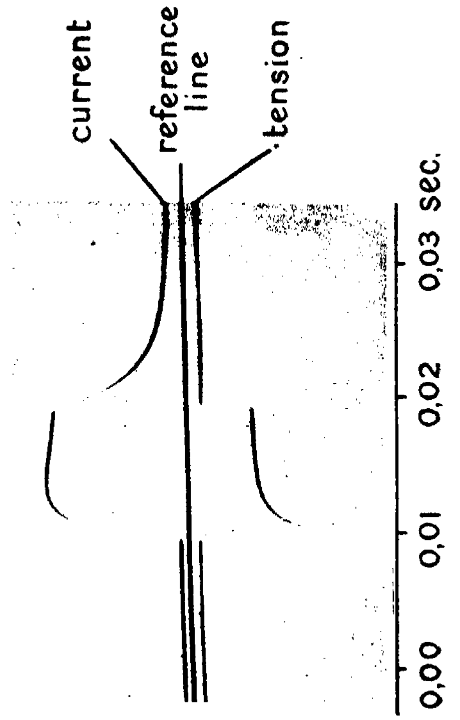
Owing to the reasons described in the beginning of this paragraph the calibration of the oscillographs was carried out in the following way:—

A resistance equal to that of the oscillograph was prepared and a current of definite value was sent through it; after switching off the current, in place of the resistance the oscillograph was introduced. By means of the big switches, the current was sent through the oscillograph for several hundredths of a second and the oscillogram taken. For verification that the current was the same, the oscillograph was again replaced by the resistance and the current checked. One of the oscillograms so obtained is shown in No. 2 (Plate 8).

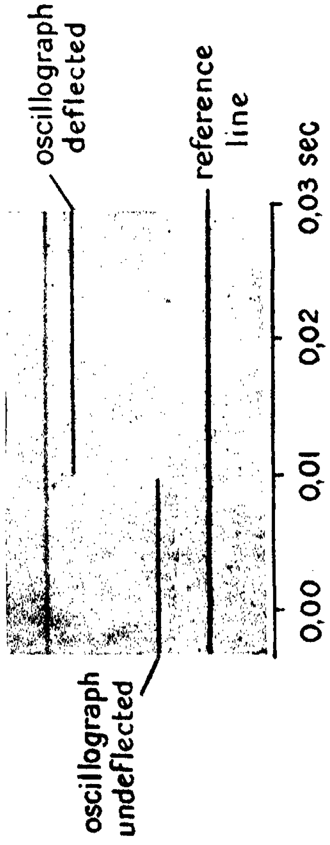
No 1



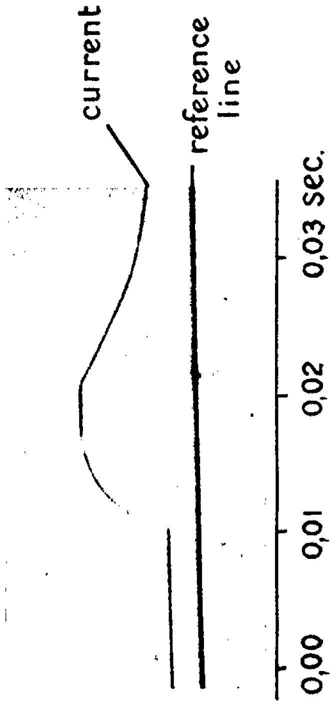
No 3



No 2



No 4



(*To face p.* 704.)

From this oscillogram it is also seen how efficient is the damping of the loop. The oscillogram shows that the oscillograph reaches its final deflection practically at once.

The proportionality between the deflection of the oscillograph and the calibrating current was verified and found to be correct to the limits of the error of measuring the current in the oscillogram (0·4 per cent.); the calibration of the oscillograph taken after an interval of time of one month showed a change of only 2 per cent., and the variation per day was no more than 0·5 per cent. This was thus the accuracy to which we could measure the current through the coil. If necessary, this accuracy could probably be increased to 0·1 per cent.

§ 4. *The Coil.*

The problem of the construction of the coil divides into three parts. The first is the choice of shape and resistance, the second the choice of the method of winding, and the third the determination of the constant.

The first part of this problem has already been fully discussed by Fabry.* He shows that the shape of the coil has no important influence on the magnitude of the field obtained. If H is the field in the middle of a coil with a circular opening of radius a, W the power of the source of electric energy available, ρ the specific resistance of the material of which the coil is constructed, η the coefficient of filling (the ratio of the total cross-section of the winding to the section actually filled with conductors), then

$$\mathrm{H} = k\sqrt{\frac{\mathrm{W}}{\rho\eta a}}. \tag{10}$$

k, the constant which depends on the shape of the coil takes different values, which in all cases of practical interest are included in the range between $k = 0{\cdot}15$ and $k = 0{\cdot}27$. From this formula it is easy to obtain a rough estimate of the field if the energy W and the radius a are given.

In our case the choice of the shape and size of the coil is somewhat more complicated. On the one hand, if we take one with many turns and of a large cross-section, it will have a large self-inductance, and in discharging the accumulator through it, it may happen that the current will reach its maximum value only at the moment when the energy of the accumulator is nearly exhausted. On the oscillograms Nos. 3 and 4 (Plate 8) discharge through two different coils, No. 2 and No. 3, are shown. Both had the shape shown in fig. 7, and the following were their details (n is the number of turns) :—

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* *Loc. cit.*

Coil No. 2. $x = 2 \cdot 7$ cm., $y = 1 \cdot 2$ cm., $2d = 3 \cdot 7$ cm., $2l = 0 \cdot 4$ cm., $n = 48$.

Coil No. 3. $x = 4 \cdot 31$ cm., $y = 2 \cdot 25$ cm., $2d = 4 \cdot 8$ cm., $2l = 0 \cdot 5$ cm., $n = 70$.

No. 3 has much larger self-inductance and the current reaches the maximum value only after 0·007 sec. : it is less efficient than the smaller coil, where the maximum is reached after 0·0025 sec., because after a hundredth of a second the power will be in all cases, as is seen from the fig. 2, about 20 per cent. less than the initial power. This indicates that small coils are more efficient than larger ones ; but, on the other hand, if the coil is small it is heated up much more quickly and the current cannot be maintained for so long a time. More difficulties are thus introduced in performing the experiment.

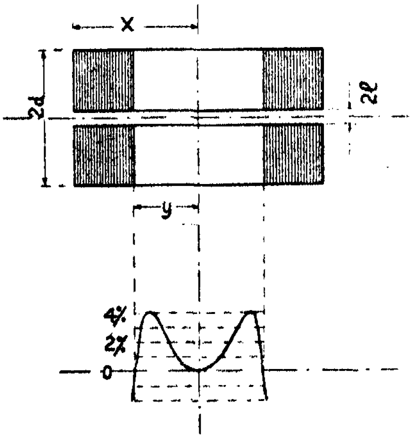

Fig. 7.

It is very difficult to take into account all these considerations. For each experiment, according to its requirements, a coil has to be chosen. After making a few coils, it is easy to find, by taking oscillograms, which is the best.

The uniformity of the field is one factor more which has to be considered in designing a coil. If the coil is very flat, then the field inside it will not be uniform. To have a field uniform to about 1 per cent., the height of the coil has to be at least twice its internal diameter, but in making it high we shall again increase the self-inductance and, in consequence, diminish the field.

When the shape of the coil is fixed it is necessary to decide what resistance shall be given to it. If it is of small self-inductance and the field is needed for a short time, then the resistance should be made equal to that of the accumulator. In the case of large self-inductances and fields of longer duration, the resistance might be taken 10 to 30 per cent. larger than in the previous case. Knowing the shape and the resistance, it is easy to calculate the number of turns.

The winding of the coil should be done in such a way as to make the coefficient of filling η as near as possible to unity. A very efficient method is shown in fig. 7. The winding is done with high-conductivity copper band insulated by a silk ribbon soaked in shellac : the coefficient of filling η was in one case about 1·2 in this example.

Finally, when the coil is made, its galvanometer constant a has to be found [α is equal to the field in gauss in the middle of the coil, when 1 ampere flows through it]. This constant can be calculated for a coil with a gap, as in fig. 7, by the following formula :—

$$\alpha = \frac{0\cdot 1\pi n}{x-y}\left[\frac{d}{d-l}\left(\sinh^{-1}\frac{y}{d} - \sinh^{-1}\frac{x}{d}\right) - \frac{l}{d-l}\left(\sinh^{-1}\frac{y}{l} - \sinh^{-1}\frac{x}{l}\right)\right].$$

This formula should give a value within 2 or 3 per cent. of the actual one. For instance, for coil No. 3 the calculated value was 10·2 as against the measured value of 10·55.

The exact determination of the constant can be done experimentally in the following way : A standard coil was taken of an internal diameter of 65 cm., very regularly wound, for which the constant a could be exactly calculated. In the middle of this, a small magnetic needle of length 1·5 mm., with a small mirror attached, was suspended on a fine quartz fibre. By means of a constant magnet placed some distance from the coil, the needle was kept in the plane of the standard coil. The coil under investigation was placed in the middle of the large coil in such a way that their planes and centres coincided. The magnetometer was also placed at the centre of the coil under investigation, the fibre passing through the gap. Currents in opposite directions were sent through both coils and were adjusted until the image from the mirror of the magnetometer thrown on a scale remained in its zero position. By measuring the ratio of the two currents it is easy from the constant of the standard coil to calculate the constant of the coil under investigation. This method is very sensitive and an accuracy of 0·1 was easily obtained.

The variation of the axial component of the magnetic field over the area of the gap in the coil under test can be found in the same way. For this purpose it was shifted in its own plane. Then the magnetometer needle, which remains in the centre of the standard coil, will be situated at different points inside the coil investigated. The variations of the axial component at all points in the gaps of coils No. 2 and No. 3 were obtained. In fig. 7 is given the variation in the coil No. 3 in the plane of the slit; it is observed that it is about 4 per cent. In coil No. 2 it was less than 1 per cent. In both cases, perpendicular to the plane of the gap, the variations of field were less than 0·1 per cent. However, this method can be applied only to coils with a gap.

§ 5. *Experiments.*

On oscillograms Nos. 3 and 4 the discharge through the coils No. 2 and No. 3 are shown. The upper curve of the oscillogram gives the current; it reaches its maximum value gradually owing to the self-inductance; and when, after a time of 0·01 sec., the coils are short-circuited, the current gradually falls, on account of the gradual dissipation of the energy of the magnetic field. The tension curve is shown below on the oscillogram No. 3; the voltage reaches its maximum value at once and afterwards gradually falls down and drops to zero when the coil is short-circuited. To measure the field inside the coil, since a was known, only the current has to be determined. This was done in two ways. First, by measuring the current oscillogram. As the resistances of the oscillograph and the shunt and the constant of the oscillograph (§3) are known, the current can be determined. Secondly, if the scale of the tension oscillogram and the resistance of the coil are known, the current can also be measured. In this case, it should be remembered that Ohm's law will hold only at the moment when the current shown by the oscillogram reaches its maximum value; for at this moment $\frac{dI}{dt}$ is equal to zero and the self-inductance term does not come in. There was an agreement of 1 per cent. between the values obtained in these two ways. The second method was not so exact as the first on account of the uncertainty in the determination of the maximum of the current, and, in general, the current was measured by the shunted oscillograph. In our experiments H was found correct to 0·5 per cent. But, if necessary, the method could be pushed to 0·1 per cent. While the accumulator was giving its full power, fields of the order of 500 kilogauss for three-thousandths of a second were obtained by discharging the battery through a coil of 1 mm. internal diameter. In coil No. 2 fields from 75 to 80 kilogauss, and in coil No. 3 from 40 to 45 kilogauss were obtained; the results with No. 3 were not so high as we estimated, because they were obtained after nine months of work by the accumulator, when its power was somewhat reduced.

The large amount of power and energy (2·5 great calories) which are yielded by the accumulator during a short fraction of a second can be easily demonstrated by fusing a copper wire 2 to 3 mm. in diameter. This gave a loud report and an intense flash of light like an explosion. Actually the current density in this usual experiment for producing magnetic fields reached the value of 100,000 amperes per square centimetre.

The mechanical forces which appeared in the coil, when the discharge was produced, on account of the interaction of the currents and the fields, were of the order of 2 or 3 tons weight, as is easily calculated. It was found that coil No. 2 during its use gradually increased its resistance, which became 4 per cent. higher at the end of the experiments than in the beginning. This increase of resistance is probably due to the expansion of the coil under the influence of the current. It is only on account of the short time during which the forces act that the coil is not pulled to pieces. This is indeed an extra difficulty which might make it impossible to obtain continuous strong fields in small coils, even if it were possible to maintain a current in them for a long time without overheating them. The forces which occur are very well demonstrated by the following experiment: Two flat coils, 3 cm. diameter, each of 22 turns, were placed one on the top of the other; between them a piece of lead and a coin were placed. After the discharge of the accumulator through the coils, a reverse of the coin was pressed in the lead.

It is interesting to discuss what would be the limit of the magnitude of short existing magnetic fields of the type described in this paper. It seems to me that the limit is mainly fixed by financial considerations. From the expression (8) we see that the strength of the field increases as the square root of the power, or, in practice, rather less rapidly, because using large powers heavier coils must be used and they will have a larger self-inductance, and so the battery will work less efficiently. I estimate that it is quite possible to arrange, on a large laboratory scale, a battery which will produce a field of the order of 2 or 3 million gauss in a coil of 1 mm. inside diameter.

There is a further possibility of increasing the strength of the field by cooling the coil with liquid air. This will diminish its resistance, and fields about 2½ times as great would be obtained. But this is only applicable to experiments of a restricted type, such as, for instance, magneto-optical experiments.

In conclusion, I would like to draw attention to the fact that in other branches of physical investigation it might be possible, by using the large power obtained from the accumulator, to increase the scope of physical research—for instance, in obtaining high temperatures, high pressures, flashes of light, etc. By transforming the current from the accumulator to a higher tension, it might be possible to obtain powerful discharges in gas tubes and X-ray flashes.

§ 6. *Summary.*

1. The possibility of obtaining strong magnetic fields for a small fraction of a second is discussed.

2. An accumulator which gives a power of the order of 1,000 kilowatts for a small fraction of a second is described.

3. Timed switches for making and interrupting strong currents up to 12,000 amperes are described.

4. An account is given of a high-frequency oscillograph (20,000 to 30,000 per sec.) for measuring strong currents occurring during a small fraction of a second.

5. The construction and measurement of the magnetic constant of coils for producing magnetic fields is discussed.

6. An account of some experiments in obtaining strong fields is given.

These experiments were performed with the continuous assistance of Mr. E. I. Laurmann, to whom I wish to express my thanks. I am indebted to Mr. H. W. B. Skinner for help in correcting the proofs of the paper. I would like also to express my gratitude to Prof. Sir E. Rutherford for providing the means with which to carry out these experiments in his laboratory, and for his constant interest in the work.

The accomplishment of this work was rendered possible by a grant from the Department of Scientific and Industrial Research.

OBITUARY NOTICES

OF

FELLOWS DECEASED.

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ALEXANDER CRUM BROWN, 1838–1922.

Crum Brown was born in Edinburgh on 26th March, 1838, his father being Dr. John Brown (1784–1858), minister of Broughton Place United Presbyterian Church. Dr. John Brown was twice married. His son by the first marriage was John Brown, M.D. (1810–1882), well known as an Edinburgh physician, but who earned a wider fame as the author of *Rab and His Friends*, *Horæ Subsecivæ*, and other literary essays. Crum Brown, the only son of the second marriage, was named after his maternal grandfather, Alexander Crum, of Thornliebank, a merchant and manufacturer of Glasgow. His mother's brother, Walter Crum, F.R.S. (1796–1867), was a chemist of note, and it is probably due to the influence of this uncle that Crum Brown's thoughts were specially directed to chemistry amongst the various subjects of his university studies.

Crum Brown's education was received in the Royal High School, Edinburgh, where he spent five years, followed by one year at Mill Hill School. In 1854 he entered the University of Edinburgh, where he graduated as M.A. in 1858 and as M.D. in 1861. During the same time he read for the science degree in London University, and in 1862 he had the distinction of being the first candidate on whom the Doctorate of Science of the University of London was conferred. After his graduation as Doctor of Medicine in Edinburgh he pursued the study of chemistry in Germany, first under Bunsen at Heidelberg, and then at Marburg under Kolbe. In 1863 he was licensed as an Extra-academical Lecturer in Chemistry by the University of Edinburgh, and in 1869 he succeeded Lyon Playfair in the Chair of Chemistry at the University, holding office till his retirement in 1908.

Crum Brown's scientific work bears a marked individual stamp. His mind was essentially philosophic and speculative, and he was specially interested in symbolic representation, as is manifest in his thesis for the M.D. degree, presented at the age of twenty-three. This was not a commonplace report of cases, but was entitled " On the Theory of Chemical Combination," and showed him to be a pioneer in scientific thought. In this thesis he expresses his purpose to sketch the history of the law of Equivalence or Substitution, and the law of Polarity, " to discuss the bearing of recent discoveries on them; and to endeavour to determine what is the form in which they may best be expressed, so as to include all the facts, and be, as nearly as possible, a strict generalisation from them." In the course of the discussion of types and radicals he evolved a system of graphic formulation in all essentials identical with that in use at the present day. His formulæ were the first to represent clearly and satisfactorily both the valency and the linking of atoms in organic compounds.

In 1864 Crum Brown published an important paper on the "Theory of Isomeric Compounds,"[*] in which, making free use of his graphic formulæ, he discussed the various types of isomerism, paying special attention to that of fumaric and maleïc acids, and in general, to compounds that are "absolutely isomeric" (*i.e.*, which possess the same constitutional formula). In continuation of his systematic work he published[†] in 1866 a paper "On the Classification of Chemical Substances by means of Generic Radicals," and in 1867 a paper "On an Application of Mathematics in Chemistry," which bears a superficial resemblance to Sir Benjamin Brodie's "Calculus of Chemical Operations," but differs from it in method, object, and result. He uses a functional notation to express certain general and serial relations in those cases where the common atomic notation is inconvenient or obscure.

Although Crum Brown apparently never contemplated the practice of medicine, his training as a medical student gave him an interest in physiology and pharmacology which led him to collaborate during 1867–8 with T. R. Fraser, a distinguished medical graduate a few years younger than himself, in a pioneering investigation of fundamental importance on the connection between chemical constitution and physiological action.[‡] Their method consisted "in performing upon a substance a chemical operation which shall introduce a known change into its constitution, and then examining and comparing the physiological action of the substance before and after the change." The operation considered was the addition of ethyl iodide to various alkaloids, the iodides (and the corresponding sulphates) thus obtained being compared with the hydrochlorides of the original alkaloids. Striking regularities were observed, amongst others "that when a nitrile [tertiary] base possesses a strychnia-like action, the salts of the corresponding ammonium [quaternary] bases have an action identical with curare."

Crum Brown's name was now well known and in his application for the Edinburgh Chair in 1869 he received the support of nearly all the prominent chemists of this country, and many of the Continent.

For some time after his University appointment he published little, but in 1873 he began a series of investigations of the organic sulphur compounds,[§] particularly derivatives of trimethyl-sulphine, which occupied him for several years, after which there was an intermission in his scientific output. In 1890 he entered a new period of chemical activity. A theoretical paper on the relation of optical activity to the character of the radicals united to the asymmetric carbon atom[||] was published, simultaneously with Guye's memoir on the same subject. About the same time began the series of researches on the synthesis of bibasic acids by the electrolysis of ester-salts.* In 1892 he published, in conjunction with John Gibson, the well-known rule for determining the position in the benzene nucleus taken up by an entering radical with respect to one already present.†

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[*] 'Trans. Roy. Soc. Edin.,' vol. xxiii, p. 707.

[†] 'Trans. Roy. Soc. Edin.,' vol. xxiv, p. 331.

[‡] 'Trans. Roy. Soc. Edin.,' vol. xxv, pp. 151 and 693.

[§] Crum Brown and Letts, 'Trans. Roy. Soc. Edin.,' vol. xxviii, p. 571, and various papers in 'Proc. Roy. Soc. Edin.'

[||] 'Proc. Roy. Soc. Edin.,' vol. xvii, p. 181.

No mention has been made of minor chemical papers dealing with practical matters, nor of the numerous and interesting addresses which he from time to time delivered. Amongst them a very clear account of the rusting of iron may be noted.‡ His view of the position of chemistry in the domain of the mathematical-physical sciences is stated in his presidential address to the Chemical Section of the British Association in 1874: "One thing we can distinctly see—we are struggling towards a theory of Chemistry. Such a theory we do not possess. What we are sometimes pleased to dignify with that name is a collection of generalisations of various degrees of imperfection. We cannot attain to a real theory of Chemistry until we are able to connect the science by some hypothesis with the general theory of Dynamics. . . . Chemistry will then become a branch of Applied Mathematics, but it will not cease to be an experimental science. Mathematics may enable us retrospectively to justify results obtained by experiment, may point out useful lines of research, and even sometimes predict entirely novel discoveries, but will not revolutionise our laboratories. Mathematical will not replace Chemical analysis."

Crum Brown had forty years ago very modern views as to crystal structure (Art. "Molecule," 'Encyclopædia Britannica,' 9th ed., 1883): "It is perhaps scarcely correct to speak of a molecular structure of [crystalline] solids at all. Solids are no doubt composed of atoms and those atoms are evidently arranged in what may be called a tactical order. When the solid is fused or dissolved or volatilised, it breaks into molecules, each repetition of the pattern being ready to become an independent thing under favourable circumstances. It may be urged that the cleavage of crystals indicates that they possess a molecular structure, but a tactical or pattern-like arrangement of atoms may easily be supposed to present planes of easier separation without the assumption of really independent molecules." Many years before the work of Laue or Bragg, Crum Brown, in conversation with the writer, mentioned that he had constructed a model of the structure of sodium chloride, each chlorine atom having six equidistant sodium neighbours and each sodium atom six equidistant chlorine neighbours, the type of structure being that now attributed to the crystalline salt.

Crum Brown never lost his interest in physiology, and at various times he made valuable contributions to that science. One of these was a study of the sense of rotation and the function of the semi-circular canals of the internal ear* (1873–74). His work was contemporaneous with that of Mach and Breuer, but his explanation went beyond theirs, suggesting the function of the ampullæ and showing how complete perception of rotation could be secured by the actual arrangement of the canals in the two ears. The relation between the movements of the eyes and the movements of the head also engaged his attention, and on this subject he wrote several papers. The analysis of vowel sounds, too, at one time interested him, and he invented a "talking bottle" which, when blown, emitted vowel sounds varying with the stopping of the holes with which it was provided.

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* Crum Brown and Walker, 'Trans. Roy. Soc. Edin.,' vol, xxxvi, p. 211; vol. xxxvi, p. 361.

† 'Chem. Soc. Trans.,' vol. lxi, p. 367.

‡ 'Jour. Iron and Steel Inst.,' 1888, p. 129.

Several published papers show his serious attention to certain branches of mathematics; for example, one on interlacing surfaces,† and another on the partition of a parallelepiped into tetrahedra, the corners of which coincide with the corners of the parallelepiped.‡ A favourite hobby was the practical construction of three-dimensional models, both crystallographic and mathematical, a gluepot on the hob and a plentiful stock of cardboard being recognised features of his retiring room in the University. In literature his reading was extensive, and his knowledge of languages, ancient and modern, was altogether exceptional.

A man of his great and varied gifts could scarcely prove other than a stimulating teacher. His lectures on organic chemistry to advanced students were revelations of the working of scientific method. He selected a few topics and dealt with them in full detail, never letting the student lose sight of the end to which the researches he described were directed, nor of the logical thread running through them. He delighted in analogies and parables, and exercised the greatest ingenuity in seeking from familiar life parallels to the scientific lesson which he wished to inculcate. A characteristic example may be found in his Presidential Address to the Chemical Society,§ where he likens the behaviour of a quantity of salt in solution to the doings of a cattle-holding community.

His turn for business was almost as notable as his talent for speculative thought. Outside the University, his Church and the Royal Society of Edinburgh claimed his chief practical interests. In Synod and Assembly he was eagerly listened to for the pith and wisdom of his utterances. His service on the Council of the Royal Society of Edinburgh extended to forty-four years in all, during twenty-six of which he acted as one of the secretaries and for six as a vice-president. The Society awarded him the Makdougall-Brisbane Prize for the period 1866–8 (in conjunction with Dr. T. R. Fraser), and the Keith Prize for the period 1873–5. His loyalty to the Society, in whose Transactions and Proceedings he published nearly all his researches, had no doubt something to do with the scant recognition of his work, their circulation amongst chemists being very limited. He was elected a Fellow of the Royal Society in 1879, and had honorary degrees conferred on him by all four Scottish Universities. He occupied the Presidential Chair of the Chemistry Section of the British Association in 1874 and of the Chemical Society in 1891–3.

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* 'Proc. Roy. Soc. Edin.,' vol. viii, pp. 255 and 370; vol. xv, p. 149.

† '*Ibid.*, vol. xiii, p. 382.

‡ 'Trans. Roy. Soc., Edin.,' vol. xxxvii, p. 711.

§ 'Chem. Soc. Trans.,' vol. lxi, p. 481.

Crum Brown presented the refreshing and fascinating contrast of a simple character combined with a brilliant and subtle intellect. He possessed a keen wit, tempered by the most delightful pawky humour; being besides a born raconteur, he shone in social gatherings, especially at his own hospitable table. He was generous and kindly, and his great learning was accompanied by a fine modesty.

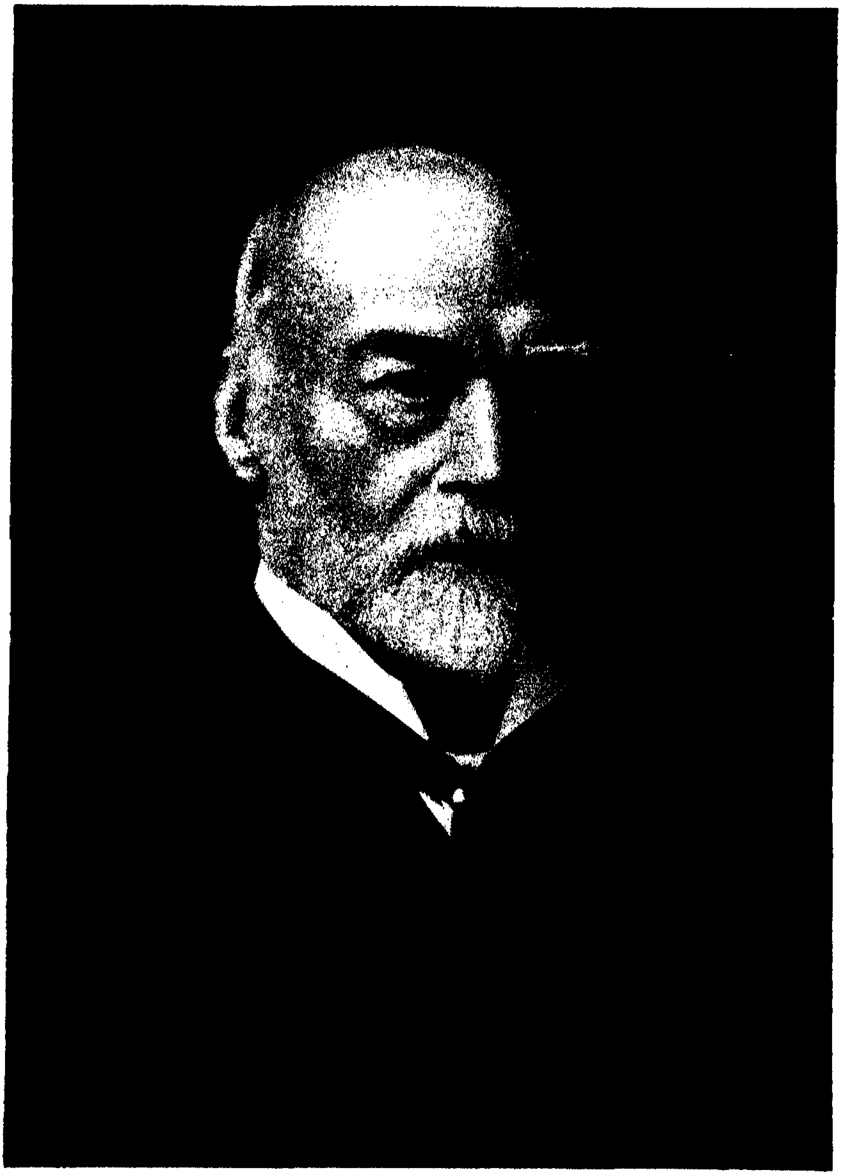
A pair of dark, sparkling, deep-set eyes formed the most striking feature of his appearance, and were a fit index of his vivacious temperament. Though physically not very robust, he spent much of his holiday time in tramping in the Highlands and on the Continent, and was rarely ill. He married early in his professional life Jane Porter, a daughter of the Rev. James Porter, Drumlee, Co. Down, whose death two years after his retirement from University duties overshadowed the last decade of his life. Failing bodily health confined him to the house, and for over seven years he had most unwillingly to regard himself as an invalid. His mind lost little of its activity. He read much and amused himself with original methods of knitting. He enjoyed conversing with his old friends, and even when increasing weakness made this somewhat of an effort for him, he would still, with an inextinguishable twinkle of the eye, retail some quaint story or interesting reminiscence. He died peacefully on 28th October, 1922, leaving to all who knew him a legacy of very pleasant memories.

J. W.

THOMAS HENRY TIZARD, 1839–1924.

The death of Captain T. H. Tizard, C.B., F.R.S., R.N., occurred on 17th February, 1924, at Kingston-on-Thames, at the age of 85. Entering the Navy as Master's Assistant 70 years ago, he served in the Baltic during the Russian War, 1854–6. On promotion to 2nd Master, in 1860, Tizard received his first appointment in the Surveying Service and joined H.M.S. "Rifleman" in China. Seven years' experience of surveying the reefs and shoals abounding in the South China Sea between Singapore and Manilla, laid the foundations of his subsequent reputation as an accomplished surveyor. For three years he was in command of the schooner "Saracen," acting as tender to the "Rifleman." He was promoted to the rank of Master in June, 1864, and three years later was invalided home suffering severely from dysentery. As Navigating Lieutenant and Senior Assistant Surveyor of H.M. Ships "Newport" and "Sheerwater," commanded by Captain (later Sir George) Nares from 1868 to 1872, he directed the laying of a submarine cable between Malta and Alexandria and was engaged in a much-needed survey of the Gulf of Suez for the benefit of the vast volume of shipping about to use the new canal route through the Red Sea. During this time it occurred to him to bring out the "Table of Chords"; this is in daily use on board every surveying vessel. An interesting and important series of observations on the surface and undercurrent in the Straits of Gibraltar set at rest the vexed question of movement of those waters.

Towards the end of 1872 the appointment of Captain Nares to command the famous "Challenger" Expedition led to Tizard's transference to the "Challenger." An excellent surveyor and navigator, a man of strong personalty and resourcefulness, and a master hand at handling a ship, a better selection could not have been made. This appointment now opened to him the great opportunity of his life in bringing him into close touch with oceanography and its leading professors. The "Challenger" Expedition for the investigation of the physical conditions of the ocean and the distribution of marine life was an epoch in oceanography, resulting in a vast increase of knowledge and in the progressive improvement of apparatus and methods of research. As Navigating Officer and Chief Assistant Surveyor, Tizard's duties involved collaboration with the leader of the expedition and the chief of the scientific staff in decisions bearing on the carrying out of the objects of the expedition. Within the broad outlines of the Instructions drawn up by the hydrographer of the Admiralty and the Royal Society Committee appointed for that purpose, the organisation of the work of each cruise, the stations to be occupied and the nature of the observations suitable for each station, necessitated consultations



in which Tizard took a prominent part. The placing of the ship in the positions decided upon and their accurate determination astronomically, would be the ordinary duty of the navigating officer, but this was only a small portion of Tizard's activities. From the outset he closely identified himself with every object with which the Expedition was concerned. As time went on the influence he exerted was increasingly apparent, and on the change of captains, which took place when Captain Nares left the ship to take command of the Arctic Expedition in 1875, Tizard's services to the "Challenger" Expedition had become so indispensable that no question of his being spared for the Arctic could arise. The Expedition would never have been the success that it was, but for the ability and cheeriness of Tizard.

Promoted to the rank of Staff Commander in July, 1874, he remained in the "Challenger" until her paying off in 1876, and was for three years employed at the Admiralty on the narrative of the voyage and its oceanographical and hydrographical results, together with a contribution to the meteorology of Japan. Little at that time was known about the latter, but from the meteorological records kept for a number of years at each of the lighthouses and lightships a very valuable series of observations had been collected. These observations were analysed and tabulated by Tizard, and from the mean monthly results diagrams were constructed showing the yearly curves.

In 1879 Staff Commander Tizard again resumed active surveying duties afloat, serving in the "Porcupine" on the survey of the coast of England before taking charge of the survey himself the following year. From 1880–82 he was in command of the hired vessel, "Knight Errant," and in the latter year commissioned a new vessel, H.M.S. "Triton," for surveying work on the east coast of England. During the nine years that he held this command he wrote many papers of scientific value and interest, some of which were published by the Admiralty. One of the earliest of these, on deep-sea exploration in the Faroe Channel in 1882, was read at the Royal Society and the Royal Society of Edinburgh, and in it Tizard showed that his observations established the existence of a continuous ridge across the Faroe Channel, which was named "Wyville-Thomson Ridge." This ridge separates the cold from the warm area, and had been predicted from the "Challenger's" report as far back as 1876. Tizard thoroughly investigated it by means of cross-sections, at each end of which serial temperatures were observed and diagrams constructed showing the distribution of the temperature from the surface to the bottom, the form of the ridge, &c., besides obtaining a series of dredgings and trawlings on top of and on each side of the ridge.

The fact was also established that there is a regular interchange of the water across the Wyville-Thomson ridge, the Atlantic water flowing north-east into the Arctic basin on the surface and so far down as the ridge permits; whilst over the deepest part of the ridge there is a small outflow of Arctic water into the Atlantic, which, though of infinitely less volume than the water moving north-east, yet appears to be sufficient to enable the bottom water of the Arctic basin, immediately adjacent to the ridge, to retain its coldness.

A lecture on "Marine Surveying," delivered at the School of Military Engineering, Chatham, was printed in the Professional Papers of the Corps of Royal Engineers. Tizard's report on his survey of the outer part of the Thames Estuary, carried out in 1889, contains information on the tidal datums used at various places on the East Coast of England and Scotland during the period covered by his survey. Two years later he compiled and published 'Notes on the Tidal Datums and Levels on the River Thames and Estuary,' thus bringing together in a convenient form for reference full information on tidal datums over a large part of British coasts.

In 1890, Tizard published in 'Nature' an interesting and highly important article on "The Thames Estuary," in which he gave an account of the changes in the channels of the estuary from the commencement of the nineteenth century. He shows these changes to be of two kinds, namely, permanent changes and periodic changes, and illustrates them by a series of diagrams. The formation of the banks of the estuary and the influences operative on them are also dealt with, and the interesting phenomenon of the opening up and disappearance of swatchways, with special reference to Duke of Edinburgh Channel, is discussed. The article deals very fully with questions affecting the estuary of the Thames, and is one of great permanent value to all those whose duty it is to maintain the channels in the estuary of a river of such national importance.

Of his other writings, an article in 'Nature' on "Sumner Lines" may be mentioned; an article on "Arctic Exploration" and a chronological list of the officers conducting British maritime discoveries and surveys, together with the names of the vessels employed, from the earliest times until 1900, is an interesting compilation.

Tizard attained the rank of Staff-Captain in February, 1889. Two years afterwards he was selected for the position of Assistant-Hydrographer of the Navy, and was elected Fellow of the Royal Society, serving on the Council from 1902 to 1904. He was placed on the retired list, with the rank of Captain, in December, 1896, but continued to serve at the Admiralty, and in June, 1899, he was awarded the honour of a civil C.B. As a member of the Joint Committee of Royal Society and Royal Geographical Society, dealing with the equipment and instructions for the conduct of the National Antarctic Expedition of 1901–4, Captain Tizard's practical knowledge of the conditions of Antarctic navigation gained during the voyage of the "Challenger," and his wide experience on all matters connected with scientific expeditions, rendered him a particularly useful member of the Committee.

The question of the feasibility of making an alternative harbour on the eastern side of the rock of Gibraltar having been raised in the House of Commons, Captain Tizard was charged to report on the matter, in conjunction with Mr. Shield, of the Works Department of the Admiralty, and in April, 1902, proceeded to Gibraltar for that purpose. The report was rendered to the Board of Admiralty in June, for which he received a letter of thanks from the Admiralty. Captain Tizard continued to serve as Assistant Hydrographer until the autumn of 1907, when he was awarded a special pension in recognition of his valuable public services. After his retirement he continued for some time to write and edit various Admiralty publications, among which 'Tides and Tidal Streams of the British Isles' was perhaps the most important; this work he re-wrote entirely.

The last, and not the least, public service performed by Tizard was to report and prepare plans to assist the Admiralty Committee, under the chairmanship of Admiral Sir Cyprian Bridge, in 1912, to arrive at a conclusion relative to the tactics employed by Nelson at Trafalgar. The investigation and co-ordination of all records from ships' logs and other sources enabled Tizard to prepare a track chart and three plans, which the Committee in its report states to be "the first and only plans representing any phase of the Battle of Trafalgar which have been exactly drawn to scale, and in which the positions assigned to particular ships in the British Fleet have been settled in accordance with the evidence contained in the logs and journals." A year or two before his death, Tizard received a further mark of recognition from the Board of Admiralty by the award of a Greenwich Hospital Pension.

Tizard had the power of great concentration of thought and application, together with a well-balanced judgment, due to habitual caution. His chief recreation was reading, and his geographical knowledge was world-wide. Gifted with a retentive memory, he was able during his service at the Admiralty to utilize to an uncommon degree the store of information to be derived from a close study of the Admiralty Sailing Directions. He was always ready to explain any scientific difficulty that occurred in the mind of a brother officer, and with his keen sense of humour was a genial companion and messmate.

Captain Tizard married in 1881, Mary Elizabeth, daughter of W. H. Churchward, C.E., who survives him.

A. M. F.

HERBERT McLEOD, 1841-1923.

PROF. HERBERT McLEOD, who died on October 1, 1923, was the son of Bentley McLeod, a brewer, and was born at Stoke Newington on February 19, 1841. He was educated at Stockwell Grammar School and at a private school at Deal, and in 1855 came to London and began the study of chemistry at the Panopticon under Prof. G. F. Ansell. In 1856 he entered the Royal College of Chemistry as a student under Prof. A. W. Hofmann, to whom he became Junior Assistant in 1858. From 1860 to 1871 he was Assistant Chemist in the Royal School of Mines under Profs. A. W. Hofmann and E. Frankland, and in the latter year was appointed Professor of Chemistry in the Royal Indian Engineering College at Coopers Hill, and held that position until 1901, when he was retired.

He was elected a Fellow of the Chemical Society in 1868 and a Fellow of the Royal Society in 1881, and was a member of Council from 1887 to 1889. He was a Fellow of the Institute of Chemistry and a member of the Society of Chemical Industry. He was also a member of the Society of Telegraph Engineers and a member of the German Chemical Society, and was an original member of the Physical Society of London. He was President of the Chemical Section of the British Association at the Edinburgh Meeting in 1892, and was made an Honorary Graduate, LL.D., of St. Andrews University in 1907.

He wrote, in conjunction with Prof. E. Frankland, the preliminary report of the Committee appointed for the determination of the gases existing in solution in well waters—'British Association Report,' 39, 1869. In 1874 he revised the fifth edition of the late William Allen Miller's 'Elements of Chemistry,' and in 1877 Part I of the sixth edition of that work.

He contributed the article on "Specific Gravity" to the first edition of the 'Dictionary of Applied Chemistry' (Longmans, Green and Co.), 1905, and was the author or joint author of a large number of papers in the 'Proceedings' and the 'Philosophical Transactions.'

McLeod was an excellent teacher and a good lecturer, sound, accurate, and well informed. As befitted the lecturer's assistant of Hofman and Frankland, his lectures were admirably illustrated by experiments. He was an expert manipulator, and a demonstration rarely failed in his hands. Indeed, experimental illustration in connection with teaching became almost a passion with him, and he spent much time and trouble in devising suitable demonstrations.

In 1902 McLeod undertook the direction of the Royal Society's 'Catalogue of Scientific Papers,' having already given many years of arduous work to this undertaking, and no selection could have been more opportune. He had already accepted the responsibility of reading the Catalogue proofs as far back as 1888, and in addition to this work he also prepared the subject-index to its papers dating between 1800 and 1900. He brought to the task a meticulous sense of accuracy, and was an ideal bibliographer—careful, patient, and painstaking. When ill-health in 1915 necessitated his retirement from further active participation in this work, he had seen the Author Catalogue for the period 1883–1900 in great part through the press.

McLeod is perhaps best known for his apparatus for the measurement of low pressures of gas, which has proved of the very greatest service when estimating the pressure of a gas when its tension is so low that the indication of the barometer cannot safely be relied upon. His Sunshine Recorder, in which the sun's light and heat from its unclouded disc are concentrated by means of a glass ball on prepared paper, whereby the duration of the sunshine is indicated by the trail of charred paper, is also well known, and is in very general use.

In 1888 McLeod married Amelia Sarah, daughter of John Woodley, brewer's cooper, of London. She survives him, together with her three sons and two daughters.

T. E. T.

JOHN ALLEN HARKER, 1870–1923.

Dr. Harker was born at Alston, Cumberland, in 1870, the son of the Rev. John Harker, Congregational Minister. He was educated at Stockport Grammar School and the Owens College, Manchester, of which he became Dalton Chemical Scholar and Berkeley Fellow in Physics. He obtained the degree of Ph.D. after a Research Course at Tübingen.

Towards the end of the last century it was realized by Sir Andrew Noble, among others, that we in England were without any temperature standards above 100° C. Callendar and Griffiths had developed the platinum thermometer and shown how to standardize it over a wide range by calibration at three temperatures, and its utility for high-temperature work had been pointed out.

Holborn, at the Reichsanstalt, working with Day, was engaged in his comparison of the gas thermometer with thermo-couples with a view to using these for high-temperature work, while Chappuis was carrying out experiments connecting the mercury standards of the Bureau des Poids et Mesures with the air thermometer.

The suggestion was made that a series of platinum thermometers should be included in the comparison, and the Kew Committee, helped by the generosity of Sir Andrew Noble, selected Harker for this work. After testing his apparatus at Kew, he settled at Sèvres, and there carried out, along with Chappuis, his well-known investigation, in which the temperature range was extended to 200° C. and Callendar's difference formula shown to hold with a high degree of accuracy. He had previously been engaged at Kew installing, under the supervision of Griffiths, the apparatus required for platinum thermometry in an outbuilding attached to the room used for testing clinical thermometers. On the completion of his work at Sèvres he returned to Kew, and on the establishment of the National Physical Laboratory at the end of 1899 became a member of the staff, along with Dr. Chree and others working at Kew.

The transfer to Teddington delayed his work, but in due time he was installed at Bushy House as Head of the Heat Division. As a gift from Sir Andrew Noble an air thermometer, a replica of that used by Holborn and Day, had been obtained, and Harker set about extending the range of comparison with platinum thermometers up to 1,100° C. The paper giving an account of his work appears in the 'Philosophical Transactions' for 1904.

More work on measurement of high temperatures followed. Harker was appointed Joule Student of the Royal Society, and in 1905 communicated an important paper on a new type of furnace, with a redetermination of the melting-point of platinum, for which he found the value 1,710° C. In this furnace he made use of the fact that certain refractory substances which are insulators when cold become conductors when heated, and can thus be used as the material of the furnace.

Meanwhile he continued his endeavours to apply the air thermometer to higher temperatures; the difficulty is to find a suitable container for the gas, and the search led to some interesting results, which were published in a paper with Dr. Kaye on "The Emission of Electricity from Carbon at High Temperatures," 'Royal Society Proceedings,' 1912.

Previous to this he had investigated with W. F. Higgins the methods and apparatus used in petroleum testing, and had served as the British delegate to a meeting of the International Commission for the Unification of Petroleum Products at Vienna in 1911.

He continued actively engaged in the work of his division until the outbreak of the war—for a time in 1913, on recovery from an illness, he acted as temporary Superintendent of the Eskdalemuir Observatory—when he was lent to the Inventions Department of the Ministry of Munitions and became Director of Research, being employed mainly in the organization of the work of the Nitrogen Products Committee. The Report of this Committee gives some account of his work.

In this capacity he visited Canada and the United States, and was returning on the *Andania* when she was torpedoed in 1918 off the Irish coast. His exposure on that occasion—he gave his greatcoat to a companion during some hours in an open boat—undoubtedly weakened his constitution, never very strong.

After the close of the war, on the completion of his work for the Nitrogen Committee, he returned to Teddington for a time, but very shortly started as a consulting engineer with Dr. J. F. Crowley in Westminster.

Pneumonia supervened on a chill taken early in October last, and he died after a very brief illness.

Dr. Harker married Ada, daughter of Mr. Thos. Richardson, of Alston, and leaves two sons and three daughters.

R. T. G.

GEORG HERMANN QUINCKE, 1834–1924.

Georg Hermann Quincke was born on the 19th November, 1834, at Frankfort-on-Oder and died on the 13th January, 1924. Having pursued his studies between 1852 and 1858 at Königsberg, Heidelberg and Berlin, he began his academic career as *privat-docent* at the University of Berlin in the year following that of graduation. In 1872 he was appointed to the Professorship of Physics at Würzburg, and three years later he succeeded Kirchhoff at Heidelberg.

Quincke's first two papers, of which one dealt with a geological subject, and the other with the lines of electric flow in metallic plates, were published while he was still a student. His doctor dissertation " De constantibus mercurii capillaribus " marks the first of a number of researches on surface tension to which he subsequently devoted a great deal of time and attention. Quincke was primarily an experimentalist, and up to a late period of his life he preferred to confirm or disprove the theories of others without any inclination to form any of his own. In his experiments on capillarity, as in the case of many of his researches, his main object was to determine physical constants, employing all known methods, and often introducing new ones. In the case of surface tension considerable discrepancies were found between the results arrived at by the five different methods used, and Quincke was in some cases successful in tracing the source of the discrepancies. He was perhaps the first to recognize the rapid deterioration of a surface, originally clean, when in contact with the air of a room. To avoid this source of error he introduced his now well-known method of measuring the capillary constant by introducing a bubble of air into a liquid, the upper surface of the bubble being kept in place by a glass plate covering the liquid. The vertical distance between the lowest point of the bubble and that at which the tangent plane is vertical is a measure of the required constant. But even when the air of the bubble is dust-free and pure, a slow change of the shape of the bubble takes place. This doubtless is due to an alteration of the surface tension resulting from the partial solution of the glass at the surface of the covering plate. Some controversy arose through the insistence by Quincke that the angle of contact between water and glass is not, as a general rule, zero. Even when the liquid wets the surface the film covering the glass gradually deteriorates so that we cease to deal with pure water. This was recognized by Quincke, who pointed out that the angle of contact increases with time. In capillary tubes angles as high as 29 degrees were observed.

In his optical researches, which were numerous, Quincke's predilection for questions involving molecular forces is apparent, for he deals by preference, though by no means exclusively, with surface effects. The difficulty of keeping surfaces clean is again insisted upon and the effects of contamination investigated. As showing some insight into the molecular cause of reflexion and refraction, the following passage is worth quoting*—"The reflexion of light has perhaps more similarity with the echo of sound at the boundary of a forest than is generally assumed." Our present theories are capable of dealing with the general problem of reflexion in a much more satisfactory manner than was possible at the time Quincke was occupied with the subject, and his extended investigations on elliptic polarization at reflexion from metallic or transparent bodies are therefore mainly of historical interest. He covered in his experimental work the whole range of interference and diffraction, and deserves some credit for pointing out, what even now is generally ignored, that the interference pattern observed by means of Fresnel's mirrors or the bi-prism is sensibly modified by diffraction at the boundary of the beams of light which are brought to interference. In studying the effects of gratings Quincke discovered the spurious spectra, the origin of which at the time was obscure but was subsequently found to be due to the periodicity of the ruling caused by the imperfection of the screw on which the distance between successive grating spaces depends.

Among many devices for measuring physical constants which we owe to Quincke, his methods of determining the magnetic permeability of liquids and the dielectric constants of non-conductors are the most important. If one branch of a U-tube containing a liquid be inserted into a magnetic field while the other lies outside it, a difference in the level of the two surfaces will show itself, the liquid being drawn into the magnetic field if paramagnetic, and out of it if diamagnetic, the observed difference of pressure on the two sides being proportional to the product of the magnetic force and the magnetic induction. A very large number of fluids and dissolved metallic salts were examined in this way. The same method suitably modified was used to determine dielectric constants of liquids. Changes of volume or of pressure due to the internal stresses in a magnetic or electric field were also investigated and applied to the measurement of the magnetic constants of gases.

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* 'Pogg. Ann.,' vol. 142, p. 398 (1871).

In one of his earlier researches Quincke examined electric endosmose, a name applied to the transportation of a liquid through a porous diaphragm when an electric current is made to traverse the liquid. He showed that this is a purely electrical process, the porous diaphragm only serving to facilitate the observation, but otherwise playing no part in it. He also demonstrated the converse phenomenon, a difference of electric potential being generated when an electrolyte is forced through a porous body.

During the last twenty-four years of his life, Quincke devoted himself exclusively to the investigation of certain intricate effects of surface tension, to which he attached great importance owing to their application to the formation and properties of living cells in which he firmly believed. As a starting point, he gives evidence for the existence of invisible and generally highly viscous fluid films which often separate the surfaces of separation between two liquids, or of solid and a liquid. These films may explain the periodic formation of precipitates which were first observed by F. F. Runge. Through the action of surface tension they may also be the origin of the formation of foam-like cells. The movement of protoplasm in the lower animals and plants is explained by the behaviour of white of egg at the surface of oily matter and water. Whatever may be the ultimate verdict on Quincke's views, his numerous, ingeniously planned and carefully executed experiments will always remain a valuable contribution to a complicated and difficult subject.

His last researches, of which two parts were published in 1914 and 1915, deal with the action of the thin liquid films which Quincke supposed to be formed inside glass by electrical action, and which according to him are the first effects of the electric strain, which ultimately lead to the perforation of the glass. Experimental work on this subject was continued almost to the end of Quincke's life, but owing to the cost of printing nothing further was published.

Quincke attended several meetings of the British Association and the Jubilee Celebration of Lord Kelvin at Glasgow. He had many friends in Great Britain, and was the senior Foreign Member of the Royal Society, having been elected in 1879.

A. S.

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